THE DISSOLUTION OF GOLD COLLOIDS IN AQUEOUS THIOSULFATE SOLUTIONS

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I declare that this thesis is my own account of my research and

contains as its main content work

which has not previously been submitted for a degree

at any tertiary education institute

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ABSTRACT

The kinetics of the dissolution of gold and silver colloids in ammoniacal thiosulfate solutions has been studied using oxygen, copper(II) or oxygenated copper(II) as oxidants at pH 9 - 11 and temperature 22^{o}C to 48^{o}C. The effects of the concentration of the main reagents such as copper(II), ammonia and thiosulfate as well as various background reagents have been investigated. Gold and silver colloids have characteristic absorption peaks at 530 nm and 620 nm respectively. Thus, the extent of gold or silver dissolution in different lixiviant systems was monitored using an ultraviolet-visible spectrophotometer. A comparison of the behaviour of gold colloids and powders has also been made. The beneficial or detrimental effects of silver colloid, and background reagents such as silver nitrate, and sodium salts of nitrate, carbonate, sulfite, sulfate, trithionate, tetrathionate anions have also been investigated.

Experimental results show that the relative rates and the extent of gold colloid dissolution at 25ºC in different lixiviant systems in a given time interval are in the order: oxygen-cyanide > copper(II)-ammonia-thiosulfate ≈ oxygen-copper(II)-ammonia-thiosulfate > oxygen-ammonia-thiosulfate ≥ oxygen-ammonia > copper(II)-ammonia. The analysis of electrode potentials shows that $Au(S_2O_3)_2^{3-}$ is the predominant gold(I) species in the lixiviant solutions containing oxygen or copper(II) as oxidant and thiosulfate or mixed ammonia-thiosulfate as ligands. During the reaction of copper(II) with thiosulfate in ammoniacal solution without oxygen, the measured potential using a platinum electrode represent the redox couple $Cu(NH_3)_n^{2+}/Cu(S_2O_3)_m^{1-2m}$ (n = 4 or 3, m = 3 or 2) depending on the concentrations of thiosulfate and ammonia.

The initial dissolution rates of gold colloid by oxygen in copper-free solutions show a reaction order of 0.28 with respect to the concentration of dissolved oxygen, but independent of the concentration of ammonia and thiosulfate. The reaction activation energy of 25 kJ/mol in the temperature range 25°C to 48°C indicated a diffusion controlled reaction.

The initial dissolution rates of gold colloid by oxidation with copper(II) in oxygen-free solutions show reaction orders of 0.41, 0.49, 0.60, 0.15 and 0.20 with respect to the concentrations of copper(II), thiosulfate, ammonia, chloride and silver respectively. The presence of silver(I) or chloride ions enhances the rate of gold dissolution, indicating their involvement in the surface reaction, possibly by interfering with or preventing a passivating sulfur rich film on gold surface. An activation energy of 40-50 kJ/mol for the dissolution of gold by oxidation with copper(II) in the temperature range 22°C to 48°C suggests a mixed chemically/diffusion controlled reaction. The dissolution of gold by oxidation with copper(II) in oxygen-free solutions appears to be a result of the reaction between gold, thiosulfate ions and the mixed complex $Cu(NH_3)_p(S_2O_3)^0$. The half order reactions support electrochemical mechanisms in some cases.

The initial dissolution rates of gold colloid, massive gold and gold-silver alloys by oxygenated copper(II) solutions also suggest a reaction that is first order with respect to copper(II) concentration. High oxygen concentration in solutions has a negative effect on the initial rate of gold dissolution and overall percentage of gold dissolution, indicating that oxygen affects the copper(II), copper(I) or sulfur species which in turn affects the gold dissolution. The surface reaction produces

$Au(NH_3)(S_2O_3)^-$ and $Cu(NH_3)_p^+$. The mixed complexes $Au(NH_3)(S_2O_3)^-$ and $Cu(NH_3)_p^+$ re-equilibrate to the more stable complexes $Au(S_2O_3)_2^{3-}$ and $Cu(S_2O_3)_3^{5-}$ in solution.

The dissolution of gold powder by oxidation with copper(II) in oxygen-free solutions shows the same trends as that of gold colloid. The presence of silver(I) or chloride ions enhances the initial rate and percentage dissolution of gold colloid and powder. The dissolution kinetics of gold powder and colloid follow a shrinking sphere kinetic model in solutions of relatively low concentrations of thiosulfate and ammonia, with apparent rate constants being inversely proportional to particle radius.

The best system for dissolving gold based on the results of this work is the copper(II)-ammonia-thiosulfate solution in the absence of oxygen or in the presence of oxygen. In the absence of oxygen, copper(II) 1.5-4.5 mM, thiosulfate 20-50 mM, ammonia 120-300 mM and pH 9.3-10 are the best conditions. The presences of carbonate and sulfite have a significant negative effect on the dissolution of gold. The presence of sodium trithionate shows a beneficial effect in the first two hours, while sodium tetrathionate or lead nitrate have a small negative effect and sodium nitrate showed no effect on the dissolution of gold. Silver nitrate and sodium chloride also show beneficial effects. In the presence of oxygen, copper(II) 2.0-3.0 mM, thiosulfate 50 mM, ammonia 240 mM and pH 9.3-9.5 are the best conditions.

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CHAPTER 1 INTRODUCTION

1.1 Gold cyanidation

John MacArthur and the Forrest brothers (Nagy et al., 1966) revolutionized the extractive metallurgy of gold by inventing the cyanidation process, in which gold is dissolved in aerated alkaline cyanide solutions (Eq. 1.1). New Zealand was the first country to use the cyanidation process for commercial applications in 1889, followed by South Africa in 1890, and the United States of America in 1891 (Eisele, 1988). Since then, for over one hundred years, the cyanidation process has been the most important process in the extraction of gold.

$$4Au\,(s) + 8KCN\,(aq) + O_2\,(aq) + 2H_2O = 4KAu(CN)_2\,(aq) + 4KOH\,(aq) \qquad (1.1)$$

Cyanidation has been the primary method for gold leaching throughout the world during the 20th century, due to the following advantages:

(i) cyanide is very effective for leaching gold from oxide ores and free milling ores,

(ii) cyanide can economically extract gold from ores with grades as low as 1-3 Au g/t,

(iii) the cyanidation process includes a convenient method for recovering gold from solution using carbon in pulp technology,

(iv) the theory of cyanidation and recovery of gold is well established.

However, the cyanide process suffers from three main disadvantages as described by Sparrow and Woodcock (1995), Li et al.(1995), Langhans et al.(1992), and La Brooy et al. (1994):

(i) cyanide cannot effectively extract gold from sulfide ores, complex copper manganese arsenic ores, or carbonaceous ores, due to high reagent consumption and a slow rate of gold leaching,

(ii) environmental problems arise occasionally due to the high toxicity of cyanide,

(iii) general environmental hazards may result from the disposal of cyanide-containing residues and any waste solutions.

As an example, carbonaceous ores give low gold recovery due to the adsorption of $Au(CN)_2^-$ onto carbon. As the ore-pits grow deeper, most of the oxidized gold-ore bodies in this category will be exhausted, leaving refractory primary ores. Thus, the traditional cyanidation process is facing challenges, leading to an increase in the search for alternative lixiviants (Li et al., 1995).

1.2 Non cyanide lixiviants

1.2.1 Potential lixiviants

Over the past two decades, there are over 500 references that appear related to the application of alternative lixiviants to cyanide for leaching gold (Aylmore, 2005). Researchers have investigated at least 15 alternative gold lixiviants,

which can be divided into 3 categories according to different leaching conditions, oxidants and ligands (Sparrow and Woodcock, 1995):

(i) Under low acidic or low basic conditions (pH 5 to 9), suitable lixiviants include thiosulfate, halogens, bromocyanide, bromine, iodine, sulfurous acid or bisulfite, bacteria and natural organic acids;

(ii) Under alkaline conditions (usually at pH > 10), effective lixiviants include cyanide, ammonia-cyanide, ammonia, sodium sulfide, and nitriles, with oxygen or sulfur as oxidants;

(iii) Under acidic conditions (pH < 3), lixiviants include thiourea, thiocyanate, aqua regia, with hypochlorite, chlorine, ferric, or cupric as oxidants.

Despite the research interest in non-cyanide gold lixiviants, alternative non-cyanide gold processes are still at the early stages of development. This is due to the low stability of the lixiviant due to side reactions. Table 1.1 shows the various lixiviants, for gold dissolution, reaction conditions, and references. The stability of gold(I)/(III) complexes with different ligands is a key factor in determining the use of a particular lixiviant system.

1.2.2 Stability constants of gold(I)/(III) complex species

The lixiviant systems listed in Table 1.1 show mixed-ligand systems such as ammonia-thiosulfate, ammonia-cyanide and ammonia-chloride. Table 1.2 lists the stability constants (β_n) for selected Au(I) and Au(III) complexes and standard reduction potentials at 25^{o}C. Some standard reduction potentials listed in Table 1.2 were calculated from β values using Eqs. 1.2 or 1.3, where L is ligand,

$E^o\{Au^+/Au\}$ = 1.69 V and $E^o\{Au^{3+}/Au\}$ = 1.50 V (Schmid and Curley-Fiorino, 1975).

$$E^o\{Au(I)L_2/Au\} = E^o\{Au^+/Au\} - (0.059/1)\log \beta_2 \quad (1.2)$$

$$E^o\{Au(III)L_4/Au\} = E^o\{Au^{3+}/Au\} - (0.059/3)\log \beta_4 \quad (1.3)$$

Gold(I) cyanide is the most stable complex with $\beta_2 \approx 10^{38}$. Gold(I) sulfide/hydrosulfide complexes are also very stable, with $\beta_n \approx 10^{30}$ - 10^{33}, followed by thiosulfate complexes. The reported values of stability constants for gold(I) diammine and gold(I) dithiosulfate vary within a large range of $\beta_2 = 10^{13}$ - 10^{26} and $\beta_2 = 10^{24}$ - 10^{28} respectively, and reflect the difficulties in measuring these quantities. Recent studies based on linear free energy correlations and half wave potential measurements have shown that the most acceptable values are $\beta_2\{Au(NH_3)_2^+\} = 10^{13}$ and $\beta_2\{Au(S_2O_3)_2^{3-}\} = 10^{24}$ (Aylmore, 2001; Hindmarsh and Nicol, 2001; Senanayake et al., 2003; Perera and Senanayake, 2004).

Table 1.1 *Gold lixiviants, conditions and references*

Ligand/oxidant	Other Conditions	Reference
Thiosulfate $S_2O_3^{2-}/Cu(NH_3)_4^{2+}/O_2$	pH > 9.0	Wan, 1997
Bromocyanide $CN^-/BrCN$	pH = 7	Dorr and Bosqui, 1950
Bromine Br_2/Br^-		Pesic et al., 1992
Iodine I^-/I_2	pH < 11	Qi and Hiskey, 1991
Sulfite SO_3^{2-}	pH > 7	Touro and Wiewiorowski, 1992
Bacteria/Natural Amino Acids	pH = 9.5, 30°C	Rapson, 1982
Cyanide CN^-/O_2	pH > 10 and Aeration	Nagy et al., 1966
Ammonia/Cyanide $O_2/Cu(CN)_3(NH_3)_2^{2-}$	alkaline	Zheng et al., 1995
Copper(II)/Ammonia $Cu(NH_3)_4^{2+}$	t > 150°C	Meng and Han, 1993
Nitriles/Malononitrile O_2 $CH_2(CN)_2$	pH = 9.5-12	Sandgren and Murphy, 1993
Thiourea $NH_2CSNH_2/Fe(III)$	pH = 1-2	Groenewald, 1977; Hiskey, 1981, 1988; Lan et al., 1993
Thiocyanate $SCN^-/Fe(III)$	pH = 1-3	Barbosa-Filho and Monhemius, 1994a-c
Chlorine (aqueous) Cl^-/Cl_2		Putnam, 1944
Aqua regia HCl/HNO_3		Hiskey and Atluri, 1988

Table 1.2 *Stability constants of selected Au(I) and Au(III) complexes and corresponding standard reduction potentials at 25°C*

Gold species	log (β_2)	log(β_4)	E^o (V)	pH	References
$Au(CN)_2^-$	38.3		-0.67	> 10	a
$Au(CN)_4^-$		56	0.40[m]		b
$Au(HS)_2^-$	32.8		-0.25[m]		c
$Au_2(HS)_2S^{2-}$	72.9		-0.46[m]		c
$Au(S_2O_3)_2^{3-}$	28		0.038[m]	8 - 11	d
	26		0.15		e
	24		0.274		a
$Au(NH_3)_2^+$	26		0.16	> 9	f
	19		0.57		e
	13		0.92[m]	> 9	h, i
$Au(NH_3)_4^{3+}$		59	0.33		e
$Au(CS(NH_2)_2)^+$	22		0.38		e
AuI_2^-	18.6		0.59[m]	< 4	a
AuI_4^-		47.6	0.56		g
$Au(SCN)_2^-$	17.1		0.66	< 3	a
$Au(SCN)_4^-$		10	0.64	1-3	a
$AuH(SO_3)_2^{2-}$	15.4		0.78[m]	5 - 7	a
$AuBr_2^-$	12		0.98[m]	< 4	a
$AuBr_4^-$		32	0.85		g
$AuCl_2^-$	9.1		1.15[m]	< 4	a
$AuCl_4^-$		25.6	1.00	< 4	f
$Au(NH_3)(S_2O_3)^-$	20				j

a: Smith and Martell, 1976; b: Nicol et al., 1987; c: Webster, 1986;

d: Sullivan and kohl 1997; e: Hiskey and Atluri, 1988; f: Wang 1992;

g: Marsden and House 1992; h: Hancock et al., 1974;

i: Senanayake et al., 2003; j: Perera & Senanayake, 2004;

m: Calculated from β values with Eq. 1.2 or Eq. 1.3.

1.3 Thiosulfate as an alternative lixiviant

Two recent reviews by Ritchie et al. (2001) and Aylmore (2005) presented a comparison of different non-cyanide lixiviant systems on the basis of the types of oxidant, process conditions, applications, current status, health and safety issues, as well as environmental concerns. Aylmore (2005) summarised that of all the processes available, thiosulfate and chloride leaching appear to be the most favourable to replace cyanide. Ritchie et al. (2001) concluded that thiosulfate is the most promising alternative to cyanide for the recovery of gold from ores. A brief comparison of the advantages and disadvantages of thiosulfate leaching of gold follows:

Table 1.3 *Relevant properties of lixiviants (Ritchie et al., 2001)*

Lixiviant	Stability of complex	Oxygen as oxidant	Chemical stability	Health and safety	Effect on environ-ment	Develop-mental stage	Low cost
Cyanide	+	+	0	-	-	+	+
Thiosulfate	0	-	-	+	+	0	+
Hydrosulfide	+	-	-	0	0	-	+
Ammonia	0	-*	0	0	0	-	+
Chloride	-	-*	+	+	+	-	+
Thiourea	0	-	-	0	0	0	0
Thiocyanate	+	-	+	-	-	0	0
Sulfite	0	-	-	0	+	-	+
Bromide	-	-	+	0	0	-	-
Iodide	0	-	0	+	0	-	-

* Only at elevated temperatures under pressure leach conditions.

1.3.1 Advantages

(i) Thiosulfate has very low toxicity and has been used as a fertilizer for many years due to its relatively low impact on the environment. The common thiosulfate salts (Na^+, K^+, NH_4^+, and Ca^{2+}) are biodegradable, are considered non-hazardous by Work Safe Australia (NOHSC, 1999), and are not considered to be dangerous substances by European Standards (Langhans et al., 1992).

(ii) Thiosulfate has the potential to treat a wide variety of gold ores, such as high copper ores, carbonaceous ores, and manganese containing ores.

(iii) Among the non-cyanide lixiviants, thiosulfate has accomplished high gold recoveries and fast leaching rates (Cao et al., 1992).

(iv) Thiosulfate can be generated in situ at low cost.

1.3.2 Disadvantages

(i) The thiosulfate processes require a solid-liquid separation stage in order to recover relatively high concentrations of unconsumed reagents.

(ii) The degradation of thiosulfate will increase reagent cost, while the degradation products (oxy-sulfur anions) have detrimental effects on the leaching and recovery process.

(iii) Thiosulfate leaching involves ammonia, a volatile and noxious reagent which can easily escape from open leaching vessels and contaminate the surroundings (Grosse et al., 2003).

(iv) One of the main methods for recovery of gold from thiosulfate solution is resin in pulp; this method is still under investigation (Nicol and O'Malley, 2001; 2002; West-sells et al., 2003).

(v) Thiosulfate processing involves complex gold-copper-sulfur chemistry.

1.3.3 Complexity of gold leaching process with thiosulfate

Gold reacts with ammoniacal thiosulfate in the presence of copper (II) as an oxidant, (Eq 1.4).

$$Au + Cu(NH_3)_4^{2+} + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + Cu(NH_3)_2^{+} + 2NH_3 \quad (1.4)$$

Meanwhile, copper(II) also reacts with thiosulfate, (Eq. 1.5)

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} = 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-} \quad (1.5)$$

This leads to a series of stable or metastable sulfur-oxygen species, for example, tetrathionate, pentathionate, trithionate, sulfite and sulfate, which could affect the kinetics of gold leaching (Naito et al., 1970; Byerley et al., 1973b; Byerley et al., 1975; Chu et al., 2003; Breuer and Jeffrey, 2003b).

Thus, the chemistry of the thiosulfate leaching and recovery of gold has been described as very complex by a number of authors (Abbruzzese et al., 1995; Ablimit et al., 1999; Breuer and Jeffrey, 2000b; Fung and Glastonbury, 1975; Molleman and Dreisinger, 2002; Muir and Aylmore, 2005). This is due to the

mixed ammonia-thiosulfate-hydroxide ligand system, which affects Cu(II)-Cu(I)-Au(I) speciation, and the polythionates formed during thiosulfate degradation (Byerley et al., 1973b; Aylmore and Muir, 2001a; Grosse et al., 2003; Molleman and Dreisinger 2002; Chu et al., 2003; Senanayake, 2004a; Black, 2006). The mixed complexes and polythionates affect the thermodynamics and kinetics of the leaching, separation, and recovery stages of gold.

There are many chemical and physical factors that affect the kinetics of gold leaching in thiosulfate media: (i) concentration of reagents, (ii) pH, (iii) temperature, (iv) ionic strength, (v) dissolved oxygen, and (vi) background salts. A number of reaction schemes and mechanisms for gold oxidation by ammoniacal copper(II) thiosulfate have been put forward, with little agreement amongst the different research groups (Jiang et al., 1993a; Breuer and Jeffrey, 2000b; Gong et al., 1993). A more detailed understanding of the mechanism of gold leaching by ammoniacal thiosulfate is essential for the development of ammoniacal or non-ammoniacal processes to treat different types of gold ores. The key to understanding the reaction mechanism is a detailed study of the thermodynamics and kinetics of gold oxidation in these solutions.

1.4 The use of gold colloids for kinetic studies

There are many ways to study the kinetics of leaching or oxidation of gold in a lixiviant system of interest. Previous reports on reaction rates and mechanism in thiosulfate media are mainly based on the following three methods of study:

(i) The leaching of gold ore or oxidation of pure gold metal (powder or plates).

(ii) The use of electrochemical methods to measure the rate of gold corrosion and solubilization.

(iii) The use of a rotating electrode quartz crystal microbalance to measure the dissolution rate of gold.

A summary of these methods and the relevant results are reviewed in Chapter 2.

Gold colloid has been used to study the reaction mechanism in cyanide media (McCarthy et al., 1998), leading to further investigations on developing a cyanide analyser (Hindmarsh and Nicol, 2001). Gold colloid is a negatively charged, hydrophobic sol maintained in solution by electrostatic repulsion (Goodman et al., 1981). The composition and structure of gold colloid particles prepared from $NaAuCl_4$ is illustrated in Fig. 1.1 (Hayat, 1989). It consists of an essentially crystalline gold core (Au) with surface adsorbed ($AuCl_2^-$) ions, which constitute the inner layer of the ionic double layer. In the intermicellar solution are H^+ ions, which repel one another by carrying a net electrostatic charge. In addition, the colloids in solution attract each other through van der Waals forces.

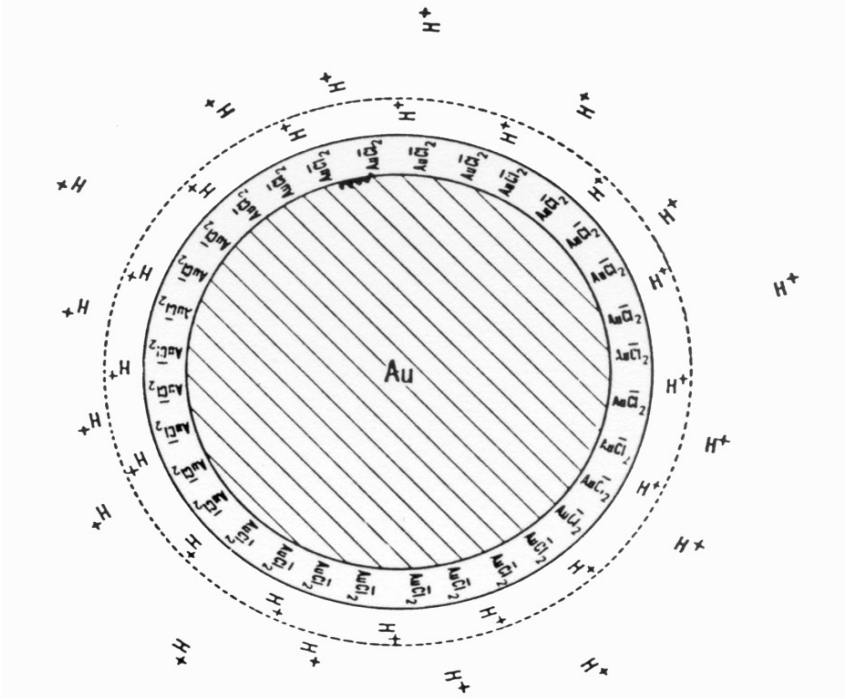


Fig. 1.1 *A diagrammatic representation of the composition of gold colloid (reproduced from Weiser, 1933; Hayat, 1989).*

The properties and characterisation of gold colloids have been well established for many years. It is well known that with increasing particle size, the heterogeneity and eccentricity of gold colloid increases. Small sized (less than 25 nm) colloidal particles are spherical, whilst large particles are more oblong in shape. The gold colloid is coloured due to a strong and sharp absorption peak in the visible range between 510 nm and 550 nm. The colour changes with particle size, from yellow-orange (less than 16 nm) to wine-red (20 nm - 40 nm), and dark red and violet (70 nm - 150 nm) (Frens, 1973). The absorbance maximum of gold colloids is proportional to its concentration. In addition, both the peak width (measured at half peak height from the absorption minimum) and the wavelength of peak absorbance increases with increasing particle size (Goodman et al., 1981).

During leaching, gold colloid particles behave in the same way as bulk gold metal, except for the large surface area. The surface area of gold colloid particles with a mean diameter of 20 nm is 15 m^2/g. This is 1000 times larger than that of gold particles of mean diameter of 20 μm in an ore (Hindmarsh and Nicol 2001). Therefore, gold colloid particles can dissolve much faster than gold metal and it changes colour from red in gold colloids to colourless gold(I) in ammonia-thiosulfate solution after oxidation. The Beer-Lambert law states that the absorption of light by a solution is proportional to the length (x) of the light path through the absorbing solution and the concentration (c) of the solution: $\ln (I_o/I) = k\ c\ x$, where I_o is the intensity of the entering light, I is the intensity of the transmitted light, and k is the absorption constant characteristic of a given system. As the dissolution progresses, the concentration of gold colloid in the solution decreases and hence the absorbance decreases. This allows the use of UV-Visible spectrophotometry to measure its concentration, to monitor the progress of gold dissolution, and to study the kinetics of dissolution of gold in copper(II)-ammonia-thiosulfate solutions or oxygen-ammonia-thiosulfate solutions.

1.5 Objectives

The main objectives of this thesis are:

(i) to study the effect of the physico-chemical factors listed in Table 1.4 on the dissolution of gold colloids,

(ii) to use electrode potentials measurement at equilibrium on gold and platinum electrodes, to examine gold(I) and copper(II)/(I) speciation,

(iii) to study the kinetics and mechanism of dissolution of gold colloids and the effect of background salts on gold oxidation,

(iv) to compare the dissolution of gold colloids, massive gold and gold ore,

(v) to test kinetic models and propose a reaction mechanism for the dissolution of gold colloids.

Table 1.4 *Factors investigated in this study*

Variable	Range
Copper(II) (mM) [a]	0.5 - 4.5
Thiosulfate (mM) [a]	10 - 100
Ammonia and ammonium/(NH_4^++NH_3) (mM) [a]	50 - 600
pH	8.9 - 11.0
Ionic strength	0.2 - 1.0
Gold colloids (mM) [a]	0.03 - 0.15
Temperature (°C)	22 - 48
Particle size (nm)	12 - 32 (gold colloids) 2250 - 7250 (gold powders)
Air/Oxygen flow rate (ml/minute)	2 - 25
Background salts (mM) [a]: $AgNO_3$, NaCl, $NaNO_3$, Na_2CO_3, $Pb(NO_3)_2$, $Na_2S_3O_6$, $Na_2S_4O_6$, Na_2SO_3	0 - 330

a. Initial concentration.

CHAPTER 2 LITERATURE REVIEW

2.1 History and recent progress on gold extraction using thiosulfate

The dissolution of gold and silver in thiosulfate media has been recognized for over a century. The first report on the use of thiosulfate for precious metal recovery dates back to 1905 in a method known as von Patera's process. In this process ammonia-thiosulfate was used for the recovery of gold from an ore subjected to a chloridising roast (Yen et al., 1998; Flett et al., 1983, Aylmore and Muir, 2001b). Following this, many decades have passed without much progress on gold leaching with thiosulfate. In 1979, Berezowski and Sefton (1979) renewed interest in the use of ammonium thiosulfate for the recovery of precious metals from a copper sulfide ore. Subsequently, studies on leaching different kinds of gold ores using ammoniacal thiosulfate lixiviant have been carried out in many countries (Langhans et al., 1992; Wan, 1997; Zipperian et al., 1988; Perez, and Galaviz, 1987; Zhang and Li, 1987; Yen et al., 1998; Murthy and Prasad, 1996; Aylmore, 2001; Feng and van Deventer, 2001; 2007a,b,c; Ji et al., 2003). Research activities have been focused on investigating the effect of physico-chemical factors such as pH, concentration of reagents, and temperature, on overall gold dissolution and recovery from different types of ores (Jiang et al., 1993a; Gong et al., 1993; Bagdasaryan, 1983; Breuer and Jeffrey, 2000b; Jeffrey, 2001; Jiang et al., 1993b; Sullivan and Kohl, 1997; Michel and Frenay, 1990; Chen et al., 1993; Jiang et al., 1993c).

A plant based on the Kerley patent (1981, 1983) had been built in Mexico using thiosulfate to leach gold, but it did not operate successfully (Gong and Hu, 1990). Perez & Galaviz (1987) pointed out that the plant could be successful if operated at pH 10 - 10.5 rather than pH 8, to avoid the problem of dissolution of iron. Newmont Gold Company (Wan and LeVier, 2003; Wan et al., 1994) set up a pilot plant for heap leaching of carbonaceous preg-robbing ores using thiosulfate. Much higher gold recoveries were achieved than with cyanide, due to the inability of the carbonaceous material to adsorb gold thiosulfate. Nicol and O'Malley (2001, 2002), Ji et al. (2003) and West-Sells et al. (2003) evaluated the effectiveness of anion exchange resins for the recovery of gold from the thiosulfate leach liquors and pulps. The separation and recovery of gold from leach solutions using ion exchange resins and carbon, solvent extraction and cementation have been discussed by Nicol and O'Malley (2001, 2002), Grosse et al. (2003), Hiskey and Lee (2003), Choo and Jeffrey (2004), Kejun et al. (2003), and Navarro et al. (2004, 2006).

Recent research work has been focussed more on the reaction mechanism and in-pulp processes for recovery of gold using lower reagent concentrations to minimise cost, for example, in heap-leaching operations (Wan and LeVier, 2003). Despite long-term interest in the chemistry of this process, progress has been particularly slow in the areas of kinetics and reaction mechanism. This is largely due to the lack of understanding of the nature of the chemical species and different types of chemical reactions involved in the thiosulfate system. Recent research papers by Aylmore and Muir (2001a), Ritchie et al. (2001), Molleman and Dreisinger (2002), Muir and Aylmore (2002), and Senanayake et

al. (2003), have addressed some issues related to speciation of Au(I)/(III), Cu(I)/(II) and polythionates, which will be examined in detail in the present study.

2.2 Gold-copper-sulfur species and electrode potentials

2.2.1 Gold and copper species

Electrochemical measurements including electrode potentials (E_H) have revealed useful information regarding the reactions involved in the thiosulfate leaching of gold. For example, Zhu et al. (1994b) and Chen et al. (1996) investigated the dissolution of gold in aqueous thiosulfate solutions using voltammetry and electrochemical impedance spectra. They established that the anodic voltametric response of a gold electrode in thiosulfate solutions includes the oxidation of thiosulfate. Zhuchkov et al. (1990, 1994) pointed out that the dissolution of gold in thiosulfate solutions could be limited by the rate of chemical dissolution of a passive surface film, possibly a hydrated oxide. Jeffrey (2001) studied the leaching of silver and gold-silver alloy in copper(II) ammonia-thiosulfate solutions using a rotating electrochemical quartz crystal microbalance and suggested that the initial rate of gold-silver allow was limited by a surface chemical reaction. Zhang and Nicol (2003) conducted an electrochemical study of the dissolution of gold in thiosulfate solutions. They found that thiosulfate ions undergo oxidative decomposition leaving a sulfur-like film on the surface of gold, which inhibits the rate of dissolution of gold and results in a low anodic current efficiency for the dissolution of gold.

The potential–pH (E_H-pH) and species distribution diagrams can be used to clarify the predominant chemical species under different E_H-pH conditions or reagent concentrations. Efforts to construct accurate E_H-pH diagrams for the gold-ammonia-thiosulfate system are hampered due to inconsistencies in published data for the stability constants (β) of the relevant complex species. For example, the reported values of β for the complex $Au(NH_3)_2^+$ differ by several orders of magnitude (Table 1.2). The published E_H-pH diagrams (Zipperian et al., 1988; Li et al., 1966) indicate that $Au(NH_3)_2^+$ is more stable than $Au(S_2O_3)_2^{3-}$ in solutions of pH > 9 (Fig. 2.1). However, there is experimental evidence to suggest that $Au(S_2O_3)_2^{3-}$ is more stable than $Au(NH_3)_2^+$ under such conditions. Li et al. (1966) measured the rest potentials of a gold electrode rotated in solutions of $Na_2S_2O_3$ or $(NH_4)_2S_2O_3$ and showed that the predominant species is $Au(S_2O_3)_2^{3-}$ rather than $Au(NH_3)_2^+$. Nicol and O'Malley (2001) also showed that $Au(S_2O_3)_2^{3-}$ loaded onto anion-exchange resins could not be eluted with concentrated ammonia solutions. Stability constants calculated from thermodynamic data also show that β_2 of $Au(S_2O_3)_2^{3-}$ is several orders of magnitude larger than that of $Au(NH_3)_2^+$ (Perera and Senanayake, 2004; Chen et al., 1993). The latter is formed only at high concentration ratios of $[NH_3]/[S_2O_3^{2-}] > 10^5$ (Perera and Senanayake, 2004).

Wang (1992) constructed E_H-pH diagrams for the Cu-NH_3-$S_2O_3^{2-}$ system and Au-NH_3-$S_2O_3^{2-}$ system at low reagent concentration. Aylmore and Muir (2001a), Muir and Aylmore (2004), Wan and LeVier (2003), and Molleman and Dreisinger (2002) have also predicted E_H-pH diagrams for this system. Wan

(1997) assumed the existence of $Au(NH_3)S_2O_3^-$, although it has not been shown in recently published E_H-pH or species distribution diagrams (Figs. 2.1-2.2) due to the lack of reliable thermodynamic data (Table 1.2). The reaction of ammoniacal copper(II) with thiosulfate ions produces copper(I) and sulfur species (Eq. 1.5). This has added to the complexity of the construction of reliable E_H-pH diagrams and elucidation of the gold oxidation mechanism. For example, recent studies by Black (2006) confirmed the existence of mixed $Cu(I)$-NH_3-$S_2O_3^{2-}$ complexes in typical thiosulfate leach liquors.

Nevertheless, typical reactions taking place under a given set of experimental conditions can be predicted from published E_H-pH and species distribution diagrams of the copper(II)-copper(I) system. For example, the following important points have been noted by Aylmore and Muir (2001a) based on Figs. 2.1a and 2.3:

(i) If pH is greater than 10, copper oxides could precipitate from solution.

(ii) The value of pH depends on the concentration ratio of $[NH_3]$ / $[NH_4^+]$, and pH 9 - 9.5 is the range in which copper(II) ammine complex is most stable.

(iii) The equilibrium between copper(II) and copper(I) influences the value of E_H, with a high Cu(II)/Cu(I) ratio giving a high value of E_H.

(iv) An appropriate concentration ratio of ammonia/thiosulfate is needed in order to stabilize the copper ions in both the Cu(I) and Cu(II) states and to maintain the availability of Cu(II) for further reaction with gold (Eq. 1.4).

(v) The leaching potential should be kept within 0.1 V to 0.5 V for stable $Au(S_2O_3)_2^{3-}$ species because at potentials lower than 0.1 V, gold cannot be

dissolved, and copper will precipitate out as a sulfide. A potential higher than 1.0 V will form $Au(NH_3)_4^{3+}$ species.

(vi) At low ammonia concentrations, ($[NH_3] < 0.1$ M) and a ratio of $[S_2O_3^{2-}] / [NH_3] > 1$, gold thiosulfate is the dominant species and will change to gold diammine with an increase in the concentration of ammonia, so high pH values favour the formation of $Au(NH_3)_2^+$.

(vii) If both thiosulfate and ammonia are low (0.1 M, Fig. 2.3), the two complexes $Cu(S_2O_3)_2^{3-}$ and $Cu(S_2O_3)_3^{5-}$ are stable over the pH range 2 - 10. Copper(II) tetraammine and copper(II) triammine can only be formed at around pH 10. At very low copper concentrations, copper(II) hydroxide will precipitate at pH > 10.5.

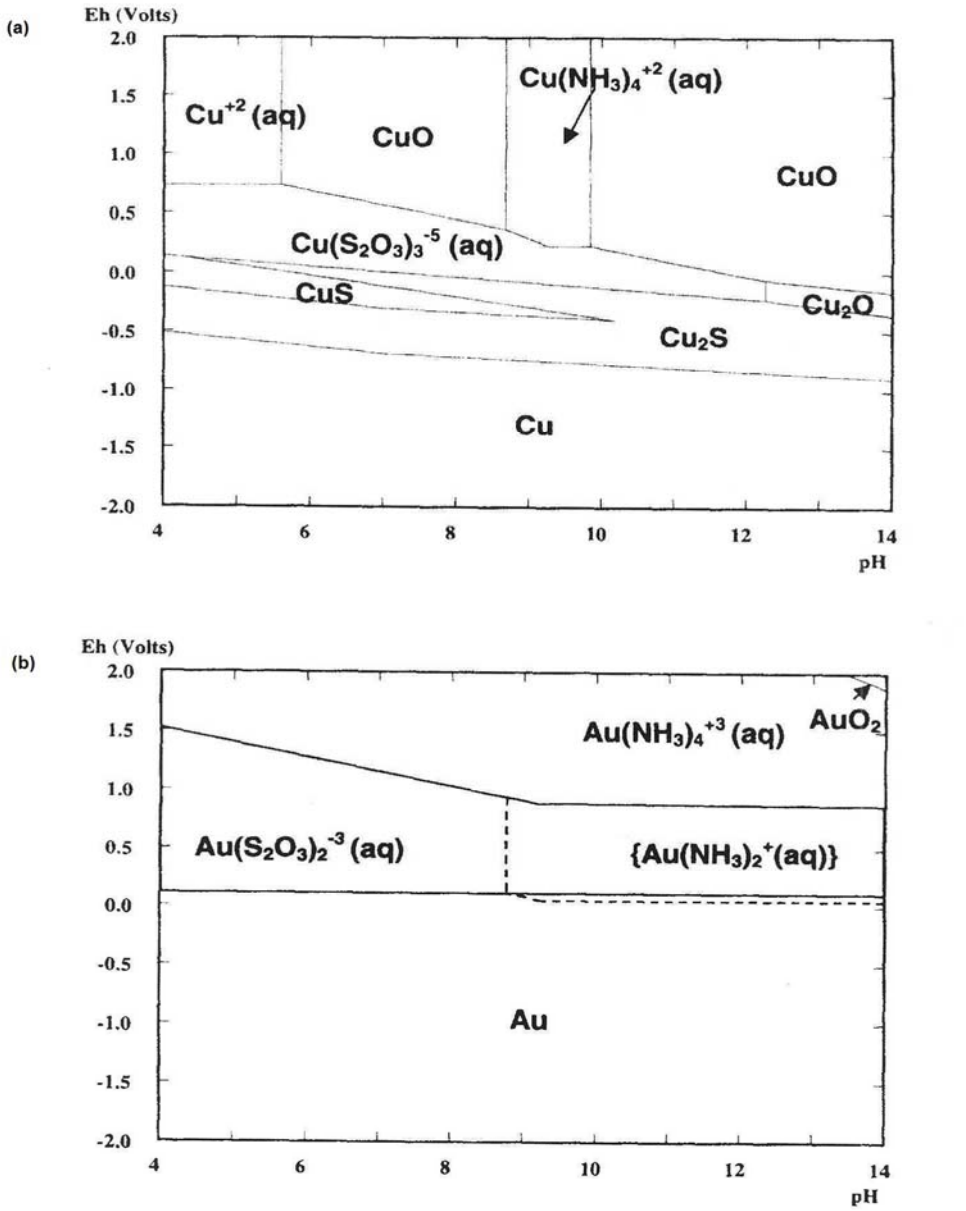


Fig. 2.1 *Potential-pH diagrams at low reagent concentrations for copper-gold-ammonia-thiosulfate systems: (a) Cu-NH_3-$S_2O_3^{2-}$ system and (b) Au-NH_3-$S_2O_3^{2-}$ system. (condition: 5 x 10^{-4} M Au, 0.1 M $S_2O_3^{2-}$, 0.1 M NH_3+NH_4^+, 5 x 10^{-4} M Cu(II)) The dotted line marks the stability region of $Au(NH_3)_2^+$, where the stability constant $\beta_2 \approx 10^{26}$ (see Table 1.3) (Aylmore and Muir, 2001a).*

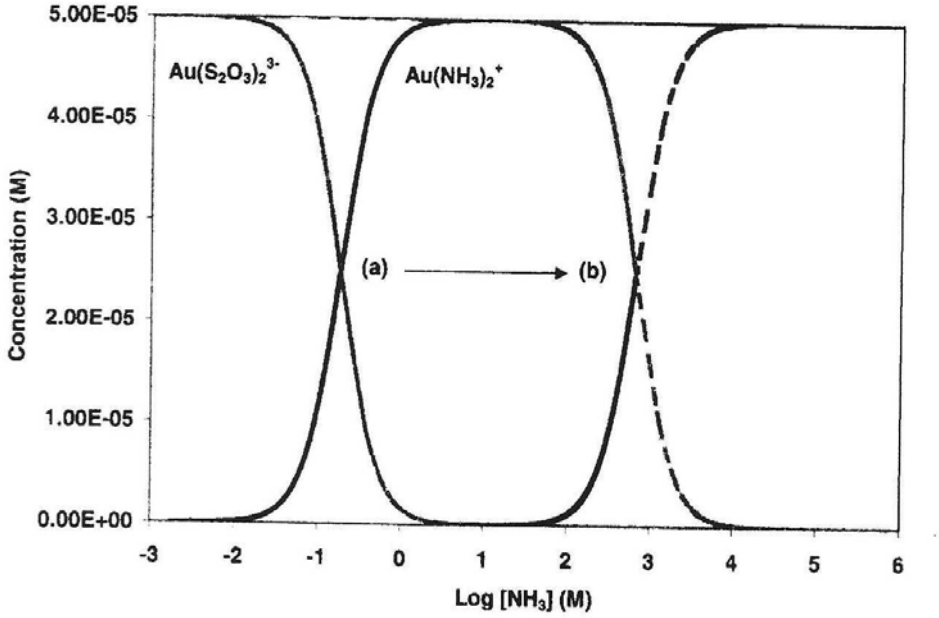


Fig. 2.2 *Effect of ammonia concentration on gold(I) species distribution (0.1M $S_2O_3^{2-}$, 5 x 10^{-5} M Au, pH = 9.5, Eh = 0.250 V, stability constant for $Au(NH_3)_2^+$ at (a) $\beta_2 \approx 10^{28}$ and (b) $\beta_2 \approx 10^{13}$, Aylmore and Muir, 2001a).*

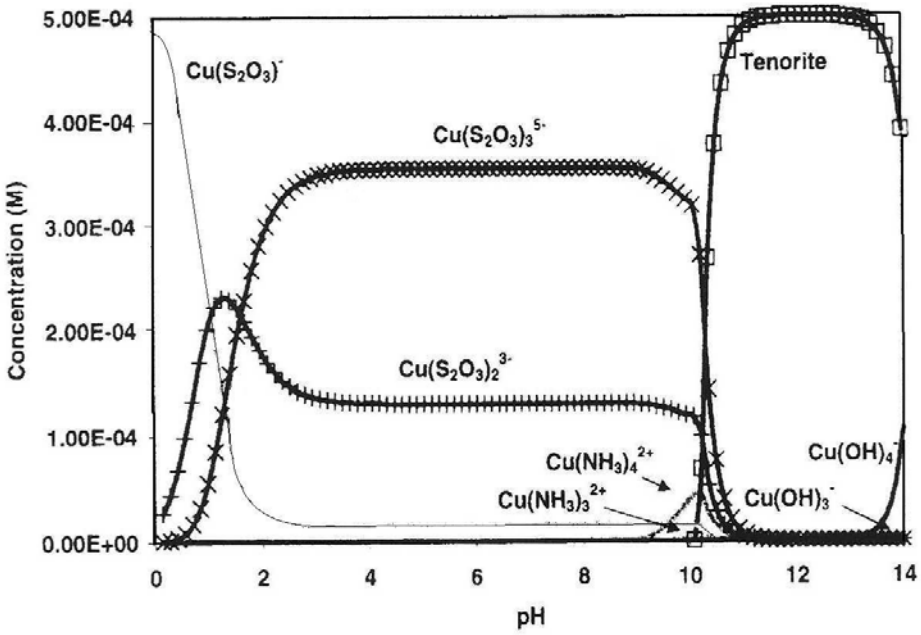
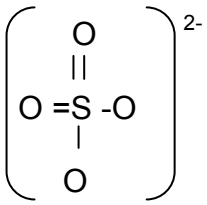


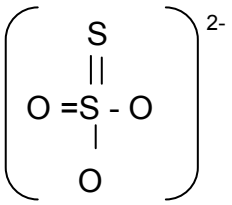
Fig. 2.3 *Effect of pH on copper(I)/(II) species distribution (0.1 M $S_2O_3^{2-}$, 0.1 M NH_3, 5x10^{-4} M Cu(II), Eh = 0.250 V, Aylmore and Muir, 2001a).*

2.2.2 Sulfur species

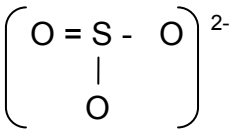
The thiosulfate ion ($S_2O_3^{2-}$) is a structural analogy of sulfate with one oxygen atom replaced by a sulfur atom (Hiskey and Atluri, 1988):



Sulfate ion



Thiosulfate ion



Sulfite ion

The central sulfur atom has a nominal oxidation state of +6 and the adjoining sulfur has an oxidation state of -2. Thus, its structure can be represented by $[S{=}SO_3]^{2-}$, where the chemical properties are dominated by the sulfide-like sulfur atom, which imparts reducing properties, strong complex tendencies and sulfide forming capabilities (Hiskey and Atluri, 1988).

In copper(II)-ammonia-thiosulfate solution, a series of stable and metastable sulfur-oxygen species (Table 2.1) may be formed in solution (Byerley et al., 1973a,b; Wan, 1997; Aylmore and Muir, 2001a; Molleman and Dreisinger, 2002; Muir and Aylmore, 2005). Some of these species are shown in Fig. 2.4, in the form of an E_H-pH diagram for the metastable S-H_2O system. It can be seen that HS^-, S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, $S_2O_6^{2-}$, $S_4O_6^{2-}$ exist**,** along with $S_2O_3^{2-}$ which occupies a narrow elongated stability field from pH 4 **-** 14 and E_H -0.6 V to 0.2 V. Tetrathionate $S_4O_6^{2-}$ is located in a large area in Fig. 2.4 and seems to be the most stable species in acidic solutions. Sulfite (SO_3^{2-}) and dithionate ($S_2O_6^{2-}$)

ions also have stability regions larger than thiosulfate ($S_2O_3^{2-}$), depending on E_H and pH.

Table 2.1 *Sulfur-oxygen species and oxidation states*

Species	Name	Oxidation State
S^{2-}	Sulfide	-2
S^0	Sulfur	0
$S_6O_6^{2-}$	Hexathionate	+1.7
$S_2O_3^{2-}$	Thiosulfate	+2
$S_5O_6^{2-}$	Pentathionate	+2
$S_4O_6^{2-}$	Tetrathionate	+2.5
$S_2O_4^{2-}$	Dithionite	+3
$S_3O_6^{2-}$	Trithionate	+3.3
$S_2O_5^{2-}$	Disulfite	+4
SO_3^{2-}	Sulfite	+4
$S_2O_6^{2-}$	Dithionate	+5
$S_2O_7^{2-}$	Disulfate	+6
SO_4^{2-}	Sulfate	+6

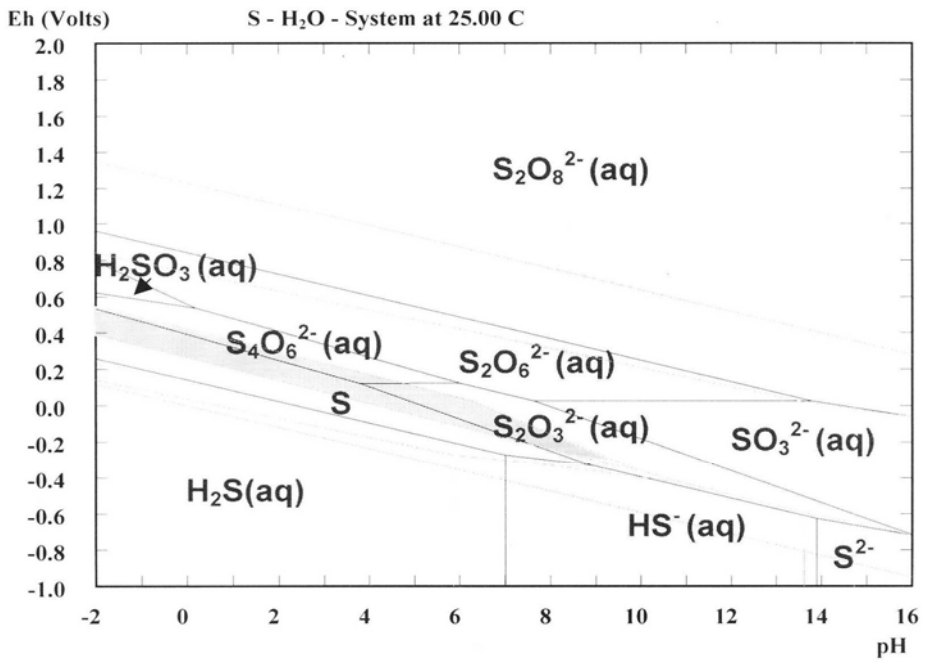


Fig. 2.4 *Potential-pH diagram for the metastable S-H_2O system at 25°C (concentration of sulfur species [S] = 1.0 M, Aylmore and Muir, 2001a).*

2.3 Production, oxidation and stabilization of thiosulfate

2.3.1 Production of thiosulfate

Thiosulfate is produced from sulfite (SO_3^{2-}), polysulfide (S_n^{2-}) and elemental sulfur (S^o), or polythionate ($S_nO_m^{2-}$), according to the reactions listed in Table 2.2. Zhu et al. (1994a) reported that the disproportionation of elemental sulfur in ammonia media produces thiosulfate and polysulfide through phase transfer catalysis (Eq. 2.3). Thiosulfate can also be generated by oxidation of polysulfides S_n^{2-}, n = 2, 3, 4,… (Chen et al., 1996) (Eqs. 2.5 - 2.7).

Table 2.2 *Summary of reactions and conditions for thiosulfate regeneration*

Reactions / References	Conditions	Eq. No
$SO_2\,(aq) + H_2O = 2H^+ + SO_3^{2-}$ $SO_3^{2-} + S^o = S_2O_3^{2-}$ (Dreisinger, 1998; Aylmore, 2001)	70 - 80°C	2.1 2.2
$4S^0 + 6OH^- = 2S^{2-} + S_2O_3^{2-} + 3H_2O$ $(x-1)S^o + S^{2-} = S_x^{2-}$ (Zhu et al., 1994a)	Phase transfer catalysis	2.3
$2SO_3^{2-} + 2HS^- + O_2 = 2S_2O_3^{2-} + 2OH^-$ (Kerley, 1981)	Heated	2.4
$Na_2S_5 + 1.5O_2 = Na_2S_2O_3 + 3S^o$ (Chen et al., 1996)	Partial oxidation	2.5
$2Na_2S + 4SO_2 + Na_2CO_3 = 3Na_2S_2O_3 + CO_2$ (Chen et al., 1996)	pH: 6.4 - 7.0	2.6
$2Na_2S_2 + 3O_2 = 2Na_2S_2O_3$ (Chen et al., 1996)	70 - 80°C	2.7

Thiosulfate ions are metastable and tend to undergo chemical decomposition in aqueous solutions. The stability of thiosulfate ions is affected by a number of factors (Dhawale, 1993; Aylmore and Muir, 2001a; Deschenes, 1998; Molleman and Dreisinger, 2002), which include:

(i) The water purity; freshly prepared thiosulfate with double-distilled water is very stable if stored in an airtight bottle.

(ii) The concentration of thiosulfate; diluted solutions (< 0.01 M) decompose more rapidly than concentrated solutions (> 0.1 M).

(iii) The pH of the solution.

(iv) The presence of certain metals or alloys.

(v) The presence of sulfur metabolising bacteria.

(vi) The presence of microorganisms and redox catalysts.

(vii) The presence of oxygen.

(viii) Exposure to ultraviolet light.

(ix) The presence of sulfite.

The high consumption of thiosulfate, when added as sodium thiosulfate or ammonium thiosulfate during gold leaching is one of the major problems in thiosulfate processes. Thiosulfate degradation in leach liquors can occur as a result of oxidation by oxygen, copper(II) or both. The degradation of thiosulfate not only results in higher reagent cost, but also leads to the formation of sulfides, which passivate gold and retard the leaching rate (Wan, 1997). Therefore, it is important to consider the possible degradation reactions of thiosulfate in the presence of the two oxidants copper(II) and oxygen.

2.3.2 Oxidation of thiosulfate by oxygen

A 5% solution of thiosulfate (by mass) has a pH of 6.0 - 8.4 at 25^{o}C and is very stable at normal pressures and temperatures. Rolia and Chakrabarti (1982) reported that under sterile laboratory conditions at pH 7, solutions of thiosulfate and polythionates were aerated for 4 months, with less than 10% change in the concentrations. Jiang et al. (1996) reported that thiosulfate solutions stirred for 24 hours at pH 6 - 12 lost less than 1% thiosulfate due to oxidation. This demonstrated that the aerobic oxidation of thiosulfate is a very slow process.

In oxygen-ammonia thiosulfate solution, the decomposition of thiosulfate as shown in Eq. 2.8 was found to be a first order reaction with respect to thiosulfate concentration (Fung and Glastonbury, 1975). Thiosulfate was also oxidized by molecular oxygen in alkaline solutions in the temperature range 75^{o}C to 87^{o}C (Rolia and Chakrabarti, 1982), and the final product was sulfate.

$$S_2O_3^{2-} + O_2 + H_2O + 2NH_3 = 2SO_3^{2-} + 2NH_4^{+} \quad (2.8)$$

$$S_2O_3^{2-} + 2O_2 + H_2O = 2SO_4^{2-} + 2H^{+} \quad (2.9)$$

$$S_2O_3^{2-} + 2O_2 + 2OH^{-} = 2SO_4^{2-} + H_2O \quad (2.10a)$$

Similar results were obtained at 100^{o}C under air pressures of 980 kPa (Gluud, 1921). The rate of oxidation of thiosulfate under pressure was increased by increasing pH, concentration of thiosulfate, oxygen pressure, and temperature (Rolia and Chakrabarti, 1982). Moreover, thiosulfate can degrade to form

sulfate and sulfur in solutions of low pH (< 9), or sulfate and bisulfide in solutions of high pH (> 9) (Dreisinger, 1998) (Eq. 2.11, Eq. 2.12).

$3S_2O_3^{2-} + 2H^+ = 4S^0 + 2SO_4^{2-} + H_2O$ pH < 9 (very slow) (2.11)

$S_2O_3^{2-} + OH^- = HS^- + SO_4^{2-}$ pH > 9 (very slow) (2.12)

2.3.3 Oxidation of thiosulfate by copper(II)

In copper(II)-ammonia-thiosulfate solutions, thiosulfate decomposition can include oxidation or reduction. The half cell reaction can be described as follows, where the final product is sulfate, sulfur or copper sulfides (Wan, 1997).

Oxidation:

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$ (2.13)

$S_4O_6^{2-} + 10H_2O \rightarrow 4SO_4^{2-} + 20H^+ + 14e^-$ (2.14)

Reduction:

$Cu(II) + S_2O_3^{2-} + 6H^+ + 6e^- \rightarrow S + CuS + 3H_2O$ (2.15)

$2Cu(I) + S_2O_3^{2-} + 6H^+ + 6e^- \rightarrow S + Cu_2S + 3H_2O$ (2.16)

In aqueous ammonia solutions without oxygen, copper(II) initially oxidizes the thiosulfate to tetrathionate ions (Byerley et al., 1973b). The exact speciation of Cu(I)/(II) complexes and the ionic charges are not shown in Eq. 2.17 due to the involvement of a number of different complexes of Cu(II) and Cu(I) shown in

Figs. 2.1a and 2.3, as well as mixed complexes of Cu(II)-NH_3-$S_2O_3^{2-}$ (Byerley et al., 1973b) and Cu(I)-NH_3-$S_2O_3^{2-}$ (Black et al., 2003; Black, 2006).

$$2Cu(II) + 2S_2O_3^{2-} = S_4O_6^{2-} + 2Cu(I) \quad (2.17)$$

Subsequently, tetrathionate ions undergo alkaline hydrolysis to trithionate and thiosulfate by raising the pH value to 11 (Muir and Aylmore, 2005; Fava and Bresadola, 1955; Foss and Kringlebotn, 1961; Naito et al., 1970, Zhang and Dresinger, 2002). The rate of oxidation is dependent on reagent concentration and pH.

$$4S_4O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (2.18)$$

The overall reaction for Eqs. 2.17 and 2.18 is:

$$8Cu(II) + 3S_2O_3^{2-} + 6OH^- = 8Cu(I) + 2S_3O_6^{2-} + 3H_2O \quad (2.19)$$

In the case of non-ammoniacal solutions in which thiosulfate is not present in large excess, or in which copper(II) is in excess, the fast redox reaction (Eq. 2.17) is followed by slower side reactions that result in the formation of Cu, Cu_2S and SO_4^{2-} (Rabai and Epstein, 1992):

$$2Cu(I) = Cu(II) + Cu(0) \quad (2.20)$$

$$2Cu(II) + S_2O_3^{2-} + H_2O + 2e = Cu_2S + SO_4^{2-} + 2H^+ \quad (2.21)$$

The rate of thiosulfate decomposition is proportional to the concentration of copper(II) and thiosulfate. The presence of ammonium sulfate and the increase in ammonia concentration results in increased stability of thiosulfate. However, an increase in temperature accelerates the decomposition of thiosulfate by Cu(II) (Fung and Glastonbury, 1975).

2.3.4 Oxidation of thiosulfate by oxygenated copper(II)

The reaction between Cu(II) and $S_2O_3^{2-}$ is catalysed by the presence of oxygen. The rate of thiosulfate oxidation in the presence of oxygen is at least forty times greater than that in the absence of oxygen (Byerley et al., 1973a). Increased oxygen percentage in air or gas flow can:

(i) rapidly oxidize copper(I) to copper(II) (Eq. 2.22),

(ii) make the direct reaction between copper(II) and $S_2O_3^{2-}$ continuous (Eq 2.17),

(iii) increase the rate of copper(II) reduction by thiosulfate to copper(I), and

(iv) rapidly oxidize thiosulfate (Breuer and Jeffrey, 2003a).

$$2Cu(I) + 0.5O_2 + H_2O = 2Cu(II) + 2OH^- \quad \text{(fast)} \quad (2.22)$$

Wensveen and Nicol (2005) investigated the kinetics of the copper-catalysed oxidation of thiosulfate in ammoniacal solutions, and pointed out that copper(I) thiosulfate complexes are very slowly oxidized while the copper(I) diammine complex is rapidly oxidised to copper(II) state by dissolved oxygen. The initial rapid oxidation of thiosulfate by copper(II) leads to a pseudo steady-state

condition. The concentration of copper(I) in the pseudo steady-state condition is relatively constant. Thus, the measured rate of oxidation of copper(I) by oxygen can be used to predict the rate of oxidation of thiosulfate.

Byerley et al. (1975) suggested a reaction mechanism involving a Cu(II)-O_2-$S_2O_3^{2-}$ complex as an intermediate, where the oxygen molecule is axially associated with the metal centre of the complex. This was proposed to cause an increase in the rate of oxidation of thiosulfate in the presence of oxygen. Experimental evidence also suggests the involvement of $S_2O_5^{2-}$ ion in the process of copper(II) catalysed oxidation of thiosulfate (Byerley et. al. 1973a). Table 2.3 is a summary of decomposition reactions of thiosulfate. It can be seen that thiosulfate can be changed to sulfur, sulfide, sulfite, sulfate or trithionate in alkaline solution, and sulfate is the most stable species. In neutral or acid solution, thiosulfate is likely to be converted to tetrathionate or sulfite and elemental sulfur. Clearly, the mechanism and decomposition pathway of thiosulfate species is complex and not yet well understand (Muir and Aylmore, 2005).

Table 2.3 *Stoichiometry of oxidative and reductive decomposition of thiosulfate*

Reactions / References	Conditions	Eq. No
$S_2O_3^{2-} + O_2 + H_2O + 2NH_3 = 2SO_3^{2-} + 2NH_4^+$ / g	NH_3	2.8
$S_2O_3^{2-} + 2O_2 + H_2O = 2SO_4^{2-} + 2H^+$ / h	T = 75-85°C alkaline	2.9
$S_2O_3^{2-} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O$ / c	$Cu(NH_3)_4^{2+}$ solution	2.10a
$1.5S_2O_3^{2-} + O_2 + 0.5H_2O = S_3O_6^{2-} + OH^-$ / c	$Cu(NH_3)_4^{2+}$ solution	2.10b
$3S_2O_3^{2-} + 2H^+ = 4S^0 + 2SO_4^{2-} + H_2O$ / f	pH < 9	2.11
$S_2O_3^{2-} + OH^- = HS^- + SO_4^{2-}$ / f	pH > 9	2.12
$2S_2O_3^{2-} = S_4O_6^{2-} + 2e$ / a	ammonia solution	2.13
$S_4O_6^{2-} + 10H_2O = 4SO_4^{2-} + 20H^+ + 14e$ / a, b, c	ammonia solution	2.14
$Cu(II) + S_2O_3^{2-} + 6H^+ + 6e = S + CuS + 3H_2O$ / a	ammonia solution	2.15
$2Cu(I) + S_2O_3^{2-} + 6H^+ + 6e = S + Cu_2S + 3H_2O$ / a	ammonia solution	2.16
$2Cu(II) + 2S_2O_3^{2-} = S_4O_6^{2-} + 2Cu(I)$ / b	alkaline	2.17
$4S_4O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$ / d	pH = 11.5	2.18
$8Cu(II) + 3S_2O_3^{2-} + 6OH^- = 8Cu(I) + 2S_3O_6^{2-} + 3H_2O$ / b	alkaline	2.19
$2Cu(I) = Cu(II) + Cu$ $2Cu(II) + S_2O_3^{2-} + H_2O + 2e = Cu_2S + SO_4^{2-} + 2H^+$ / i	excess copper(II)	2.20 2.21
$2Cu(I) + 0.5O_2 + H_2O = 2Cu(II) + 2OH^-$ / b	Oxygen	2.22
$2S_2O_3^{2-} + 0.5O_2 + 2H^+ = S_4O_6^{2-} + H_2O$ / f	pH = 7	2.23
$S_2O_3^{2-} + S_3O_6^{2-} + H^+ = S_4O_6^{2-} + HSO_3^-$ /d	pH $\leq$ 7	2.24
$S_2O_3^{2-} + H^+ = S + HSO_3^-$ / d, e	pH $\leq$ 7	2.25
$S_2O_3^{2-} = S + SO_3^{2-}$ / f		2.26
$3S_2O_3^{2-} + 6OH^- = 4SO_3^{2-} + 2S^{2-} + 3H_2O$ / e	alkaline	2.27
$2Cu(NH_3)_4^{2+} + 8(S_2O_3)^{2-} = 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-}$ / j	alkaline	2.28
$Cu(II) + S_2O_3^{2-} + 2OH^- = CuS + SO_4^{2-} + H_2O$ / g	hot solution	2.29
$2S_2O_3^{2-} + H_2O + 0.5O_2 = S_4O_6^{2-} + 2OH^-$ / c, d	$Cu(NH_3)_4^{2+}$ solution	2.30

a. Wan, 1997; b. Byerley et al., 1973a,b; c. Byerley et al., 1975; d. Naito et al., 1970; e. Huang et al., 1998; f. Dreisinger**,** 1998; g. Fung and Glastonbury 1975; h. Rolia and Chakrabarti, 1982; i. Rabai and Epstein, 1992 (non ammonia system); j. Chu et al., 2003.

2.3.5 Stabilization of thiosulfate

The high consumption of thiosulfate during gold leaching is a major problem, highlighting the importance of stabilization of thiosulfate in leaching solutions. Table 2.4 lists a series of reactions showing the formation of thiosulfate from various sulfur species. Two patents were assigned to Kerley (1981, 1983) for the addition of sulfite ions to control the stability of thiosulfate solutions during the leaching reaction, according to Eq. 2.34 in Table 2.4. Some other benefits of the addition of sulfite are as follows:

(i) Sulfite ions can react with sulfide ions in solution, preventing the precipitation of metal sulfides as shown in Eq. 2.36 in Table 2.4 (Li et al., 1995).

(ii) As described by Perez and Galaviz (1987) in their patent, an excess of sulfite may prevent the precipitation of sulfur according to Eq. 2.39 in Table 2.4.

(iii) Sulfite is an unstable substance which can be oxidized to sulfate during leaching:

$$SO_3^{2-} + 0.5O_2 = SO_4^{2-} \quad (2.32)$$

(iv) The addition of SO_3^{2-} to stabilize $S_2O_3^{2-}$ does not reduce reagent consumption, rather, the loss of thiosulfate in leaching solution is replaced by the loss of sulfite due to the reaction shown in Eq. 2.32.

Gong and Hu (1990) reported that the presence of sulfide in solution would be advantageous for the stabilization of thiosulfate (Eq. 2.35 in Table 2.4). They recommended a minimum pH of 9.5 for the copper (II) ammonia thiosulfate

system to stabilize thiosulfate. However, some experimental results contradict this suggestion. For example, Molleman and Dreisinger (2002) investigated the treatment of copper-gold ores by ammonia thiosulfate, but did not observe that sulfite and sulfate improved the stability of thiosulfate.

Hu and Gong (1991) used sulfate instead of sulfite in gold leaching to reduce the loss of thiosulfate. As the sulfate was not consumed during leaching, they suggested the reaction in Eq. 2.33 (Table 2.4) as a mechanism that would avoid reagent consumption. However, Aylmore and Muir (2001b) doubted this reaction (Eq. 2.33), because SO_4^{2-} is very stable. Thiosulfate oxidation by copper(II) occurs via mixed complexes such as $Cu(NH_3)_3(S_2O_3)^0$ (Byerley et al., 1973b). Recent studies by Chandra and Jeffrey (2004), and Wensveen and Nicol (2005) showed that the addition of sulfate retarded the reaction of copper(II) with thiosulfate as well as the oxidation of gold by copper(II) due to the formation of $Cu(NH_3)_p(SO_4)^0$. Based on kinetic studies, Wensveen and Nicol (2005) confirmed the formation of an intermediate mixed ammine/thiosulfate copper(II) complex.

Table 2.4 *Stoichiometry of the stabilization reactions of thiosulfate*

Reactions / References	Conditions	Eq. No
$SO_4^{2-} + S^{2-} + H_2O = S_2O_3^{2-} + 2OH^-$ / c	Alkaline solution	2.33
$SO_3^{2-} + 2OH^- + S_4O_6^{2-} = S_2O_3^{2-} + SO_4^{2-} + H_2O$ / d	pH 8	2.34
$4SO_3^{2-} + 2S^{2-} + 3H_2O = 3S_2O_3^{2-} + 6OH^-$ /g, d	Alkaline solution	2.35
$4SO_3^{2-} + 2HS^- + H_2O = 3S_2O_3^{2-} + 4OH^-$ / b, e	Alkaline solution	2.36
$SO_3^{2-} + S_4O_6^{2-} + HS^- + OH^- = 3S_2O_3^{2-} + H_2O$ / b	Alkaline solution	2.37
$SO_3^{2-} + S_4O_6^{2-} = S_2O_3^{2-} + S_3O_6^{2-}$ / b		2.38
$4SO_3^{2-} + 2S + 6H^+ + 4e = 3S_2O_3^{2-} + 3H_2O$ / f	heated	2.39
$2SO_3^{2-} + 2HS^- + O_2 = 2S_2O_3^{2-} + 2OH^-$ / d		2.40
$2S_4O_6^{2-} + 3OH^- = 2.5S_2O_3^{2-} + S_3O_6^{2-} + 1.5H_2O$ / a	pH = 11.5	2.41
$S_3O_6^{2-} + 2OH^- = S_2O_3^{2-} + SO_4^{2-} + H_2O$ / a	pH = 11.5	2.42
$2S_3O_6^{2-} + 6OH^- + 2O_2 = S_2O_3^{2-} + 4SO_4^{2-} + 3H_2O$ /a	pH = 13	2.43
$2S_5O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 3H_2O$ / a	pH = 13	2.44
$3S_4O_6^{2-} + 10OH^- + 2.5O_2 =$ $4S_2O_3^{2-} + 4SO_4^{2-} + 5H_2O$ / a	$[NH_3] > 2M$	2.45
$3S_4O_6^{2-} + 6OH^- + 2.5O_2 + 4NH_3 =$ $4S_2O_3^{2-} + 4SO_3NH_2^- + 5H_2O$ / a	$[NH_3] > 2M$ no air	2.46
$4S_4O_6^{2-} + 10OH^- = 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O$ / a	$[NH_3] > 2M$ no air	2.47
$4S_4O_6^{2-} + 8OH^- + 2NH_3 =$ $7S_2O_3^{2-} + 2SO_3NH_2^- + 5H_2O$ / a	$[NH_3] > 2M$ no air	2.48

a. Naito et al. (1970).

b. Dreisinger (1998).

c. Hu and Gong (1991).

d. Kerley (1981).

e. Li et al. (1995).

f. Perez and Galaviz (1987).

g. Gong and Hu (1990).

2.4 Leaching of gold

The thiosulfate system has been used to leach gold from different types of materials as listed in Tables 2.5 and 2.6. The gold ores or concentrates used in batch leaching experiments had different mineralogy, gold grade and chemical composition, so the optimum leaching conditions were also different (Table 2.7). A summary is presented as follows:

(i) For most ores, the optimum concentrations were: thiosulfate 0.1 M to 1.0 M, copper(II) < 0.1 M, ammonia 0.1 M to 3.0 M at pH 9 - 10.5 and temperatures up to 60^{o}C.

(ii) For a mild refractory ore, the optimum reagent concentrations have been reported as 0.05 M Cu(II), 0.5 M $Na_2S_2O_3$, and 6 M NH_3 (Yen et al., 1998).

(iii) The optimum reagent concentrations for a chalcopyrite concentrate have been reported as 0.05 M Cu(II) and 0.3 M $Na_2S_2O_3$ at pH = 10 (Navarro et al., 2002), which gave 94% extraction after 15 hours.

(iv) In the case of a carbonaceous ore, the optimum reagent concentrations were 0.05 M Cu(II), 0.71 M $S_2O_3^{2-}$, and 3 M NH_3 at pH 10.5 (Hemmati, 1987), which gave a gold extraction of 73%.

Table 2.5 *Different types of ores/concentrates used in thiosulfate leaching*

Ore type	Symbol in Table 2.6-2.7
Oxidized ore	(O1) - (O4)
Sulfide ore	(S1) - (S4)
Sulfide concentration	(SC)
Carbonaceous ore	(C1) - (C 6)
Refractory ore	(R1)
Chalcopyrite ore	(Cha)
Rhyolite ore	(Rh)
Gold (bearing) ore	(G1) - (G4)

Table 2.6 *Chemical composition of different types of starting material used in thiosulfate leaching**

Ore type	Particle size	S:L	Au g/t	Ag g/t	C_{org}.%	Cu %	Fe %	Si %	S_{tot} %	Al %	As %	Ca %	Zn %	Mg %	Mn %	Pb %
O1	-100 mesh	1:1	480	570	0.11	0.02	3.13	39.0	1.12	3.00	0.07					
O2			4.75	12.5			3.25	73.6		4.1		<0.005	0.13			
O3		1:10	7.0													
S1	90% < 200 mesh	1:6	62	60	0.42	3.19	28.9	38.0	20.6	5.8		0.39	0.1	0.28	0.048	< 0.03
S1			1.75	22.5		0.4	11.1		9.8				0.7	5		0.25
S2			50.4		0.42	3.19	28.9	37.95	20.6	5.75		0.39	0.1	0.28	0.048	< 0.03
S3			94.6	24		0.20	31.9		30.7	2.64		1.96	0.022	0.829	0.073	0.004
S4	66% < 200 mesh		5.0	-	-	0.22	14.7	0.002								
C1	50% < 200 mesh		8.67	-		0.02	>7	major		major	-	major	-	3.0	0.02	< 0.01
C2	-100 mesh		13.4		2.5											
C3	< 1.9 cm		1.46-3.17	0.78-1.35	0.67-2.42				0.78-1.35	2.5	0.14	5.6	0.036	2.4	0.19	0.026
C4			9-10		1.51	0.005	3.8	51.8	0.39	9.8	0.043	12.6	0.017	2.6	0.01	
C5	80% < 200 mesh	1:1.5	6.79		7.35	0.004	1.35		1.22	1.97	0.06				0.028	
C6	80% <75 µM	9:11	8.3	0.2	1.77	0.61	2.24		0.11	1.60	0.085	7.66	0.016	0.86	0.020	
R1	65% <74 µM	1:1.2	7.92	3.06	<0.25	0.37	7.6		5.62							
Cha			95	235		3.7	40.4						6.9			1.5
Rh			3	113											0.7	
G1			1.28						0.73							
G2			51.6	1												
G3			146.	293		6.20	39.2	5.85	41.1	0.25		0.39	0.25	0.29		0.46
G4			153	443		4.71	40.9	4.23	38.4	0.24		0.54	0.84	0.32		0.26

S : L= solid : liquid.

$C_{org.}$ %: Percentage of organic carbon from carbonaceous matter.

* Most ores studied have low copper except S1, S2, G3, G4.

Table 2.7 *Maximum gold leaching under optimum conditions*

Ore Type / Reference	T (^oC)	pH	NH_3 (M)	Na_2SO_3 (mM)	Retention Time (h)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	Gold Recovery %
O1 / a	Amb		0.09	6.25	48	1	0.2	83
O2 / b	60		1.68	79	2	78	0.64	93.9
O3 / c	50		0.5	1 M NaCl	2	-	0.8	96
O4 / d	Amb	≈7	-	-	48	-	0.3	98[t]
S1 / e	60	10.2	3	-	2	47	0.2	97.7
S2 / f	40		1.8-2.2	100	1.5	16	0.8-1.0	95
S3 / g	Amb	10.2	4	-	48	50	0.8	90
S4 / h	35	10-11	1.0	90	2	32	0.19	80
S5 / i	37	-	1	-	0.5	NM	0.5	82
C1 / h	60	10-11	1.0	224	1.5	64	0.27	75
C2 / j	35	10.5	3.0	100	2	50	0.9	73
C3 / k	Amb	9	0.1	-	60 days	0.5	0.1	62
C4 / l	60	11	0	-	3	0	0.1	80
R1 / m	Amb	10.2	6	-	24	100	0.5	95
Cha / n	Amb	10	1	-	15	50	0.3	90
Rh / o	50	10	4	-	1-2	0.1	2.66	70
G1 / p	60	10.5	2	0.8 M SO_4^{2-}	2.5	0.12	0.287	> 93.5
G2 / q	25	8.5-10.5	4		3	100	2	80

(O1)-(O5):Oxidized ore, (S1)-(S5): Sulfide ore; (SC): Sulfide concentration;

(C1)-(C4): Carbonaceous ore;(R1): Refractory ore; (Cha.): Chalcopyrite ore;

(Rh): Rhyolite ore; (G1) and (G2): Gold (bearing) ore;

Amb: Ambient; NM: Not Mentioned.

a. Langhans et al. (1992); b. Ji & Yu (1991); c. Li & Kuang (1998);

d. Zhang et al. (2005); e. Cao et al.(1992); f. Gong & Hu (1990);

g. Aylmore (2001); h. Bhaduri (1987); i. Block-Bolten et al. (1985);

j. Hemmati (1987); k. Wan & Brierley (1997); l. Ji et al.(2003);

m. Yen et al.(1998); n. Navarro et al.(2002); o. Zipperian et al. (1988);

p. Chai, (1997); q. Abbruzzes et al.(1995).

t. 10 mM thiourea and 3 mM Fe-EDTA.

2.4.1 Oxide ore

Langhans et al. (1992) claimed that copper-catalysed thiosulfate leaching might be competitive with conventional cyanidation methods for heap, dump or in situ leaching. They carried out statistically designed experiments to determine the optimum leaching conditions for minimum thiosulfate consumption and maximum gold extraction (O1 in Tables 2.6 - 2.7). The leaching rate was slow due to low reagent concentration, resulting in only 83% gold extraction, with 0.4 kg $S_2O_3^{2-}$ consumed per tonne of ore. In comparison, standard cyanidation gave 86% gold extraction with 0.21 kg CN^- consumed per tonne of ore. Navarro et al. (2002) also showed that leaching of gold from a sulfide concentrate using ammonium thiosulfate at pH 10 - 11 gave faster gold extraction than standard cyanidation. Ji & Yu (1991) studied gold extraction from refractory deeply oxidized mud ore and reported a higher gold recovery of 93.9% under optimum conditions (O2 in Table 2.7). Li & Kuang (1998) investigated the leaching of gold from an oxide ore and showed that the extraction of gold increased 15% when the concentration of sodium chloride added was increased from 0.2 M to 1.0 M (O3 in Table 2.7). In a recent study Xia and Yen (2005) extracted 92% of gold from a gold bearing silicate ore within three hours using a solution of 0.2 M ammonium thiosulfate, 0.9 M ammonia, 30-300 mg/L copper(II), and 8.6 mg/L dissolved oxygen at pH 10.3.

2.4.2 Sulfide ore

Cao et al. (1992) investigated the leaching of gold using a low concentration of thiosulfate in solution and achieved 95% gold extraction from auriferous sulfide ore, (S1 in Tables 2.6 and 2.7). For a gold concentrate of complex metal sulfides (G3 in Table 2.6), the gold recovery was 96% at an optimum concentration ratio of $S_2O_3^{2-}$ / Cu(II) = 10 - 15 and $S_2O_3^{2-}$ / SO_3^{2-} = 4 (Zhang & Li, 1987). Gong & Hu (1990) also reported a higher gold extraction of 95% from a sulfide concentrate containing copper(II) (S2 in table 2.6). They used a lower temperature of 40^{o}C and lower concentrations of copper(II) and ammonia, but a higher thiosulfate concentration (Table 2.7). The stripped ammonium thiosulfate solution was directly re-used in this process. In carefully controlled experimental conditions, aeration resulted in oxidation of copper(I) to copper(II), with very low thiosulfate oxidation. Molleman and Dreisinger (2002) showed that aeration is a key control parameter during the leaching of a copper-gold ore using ammonium thiosulfate. The surface aeration gave a slow but higher gold recovery, with low thiosulfate degradation. Forced aeration gave fast initial leach kinetics but lower final gold extraction, with high thiosulfate degradation. Feng and van Deventer (2007a,b) also showed the beneficial effects of oxygenation and low concentrations of sulfur species on gold leaching from sulfide ores.

Aylmore (2001) reported a gold recovery of 90% from a refractory gold-copper sulfide concentrate using ambient conditions in a 48 hour leach. However, the

reagent consumption was high: thiosulfate 36 - 70 kg/t, ammonia 5 kg/t, copper 1-2 kg/t, after leaching for 24 hours (S-3 in Table 2.7). Ficeriova et al. (2002) studied the leaching of gold from a mechanochemically pre-treated Cu-Pb-Zn complex sulfide concentrate using ammonium thiosulfate solution at pH 6 - 7 and an elevated temperature of 60^{o}C to 70^{o}C. The particle size of "as-received" sample, d_{50} = 25 μm, was reduced to d_{50} = 4.5 μm after an energy input of 202 kWh/t. The corresponding gold recovery varied from 54% to 85%. They suggested that the enhanced gold recovery was due to the increase in surface area to about 2.5 m^2/g. Feng and van Deventer (2007c) achieved a gold extraction close to 100% from a sulfide ore after 48 hours, but this was decreased to 80% in the presence of hematite due to enhanced thiosulfate degradation and gold passivation. Air injection also decreased gold leaching due to accelerated thiosulfate decomposition (Feng and van Deventer, 2007b). However, oxygen injection was beneficial when it enhanced the dissolution of host sulfides, releasing more gold from the sulfide matrices.

2.4.3 Carbonaceous ore

Due to the high affinity of carbon towards the complex ion $Au(CN)_2^-$, cyanidation cannot effectively leach gold from carbonaceous ores. However, carbonaceous material has a very low affinity for gold-thiosulfate complex ions (Wan & Brierley, 1997), so it is possible to extract gold from carbonaceous ore using a thiosulfate

lixiviant. Newmont Gold developed a bio-oxidation process for the pretreatment of low-grade carbonaceous-sulfidic refractory gold ore (C3 in Table 2.6), which cannot be heap leached with cyanide. The bio-oxidation-thiosulfate heap process was successfully practiced on a pilot plant scale. A total of 327,000 tonnes of carbonaceous-sulfidic ore, pre-treated using bio-oxidation, was leached with ammonium thiosulfate. They also reported that the concentration ratio of ammonia to thiosulfate should be kept within a certain range, so that copper can easily transfer between the cupric and cuprous state. In addition, a key factor for success was maintaining the stability of the leaching system by controlling the solution pH and redox potential (E_H).

Feng and van Deventer (2001) studied preg-robbing phenomena in gold leaching. They tested five ores (arsenopyrite, chalcopyrite, pyrite, kaolin, and quartz) that were highly preg-robbing with fast adsorption of gold cyanide. However, thiosulfate leaching greatly decreased or eliminated preg-robbing in both mineral and gold ore systems. It was found that the presence of lead(II) and zinc(II) ions could reduce preg-robbing, whereas copper(II) ions could not. Hemmati (1987) concluded that thiosulfate is chemically superior and economically more advantageous than cyanide because it was possible to extract 73% of gold from a carbonaceous ore using ammoniacal thiosulfate under optimum conditions (C2 in Table 2.6 and Table 2.7).

West-Sells and Hackl (2005) conducted a thiosulfate leach process for the treatment of carbonaceous gold ores (C6 in Table 2.6) at ambient temperature, and 70% and 78% gold was extracted in 4 hours and 24 hours respectively. All the dissolved gold was recovered by precipitation with ammonium sulfide.

In most cases, thiosulfate leaching of carbonaceous ore was carried out in a pressure autoclave at 50^{o}C to 60^{o}C to increase leaching kinetics and gold recovery. A United States Patent (Thomas et al., 1998) described gold recovery from refractory carbonaceous ores using pressure oxidation (oxygen pressure = 400-500 psia), copper(II) (10-100 ppm) and thiosulfate (10-100 mM) leaching, where 75% to 85% gold was recovered, compared with only 6% gold recovered by cyanidation. Schmitz et al. (2001) compared the results from ammoniacal thiosulfate and sodium cyanide leaching of preg-robbing Goldstrike ore and carbonaceous matter. Regardless of the preg-robbing behaviour of the parent ore, in which about 60% of gold was encapsulated in sulfides, only 40% gold was extracted from non-autoclaved ores. A much higher gold solubilization of 90% to 100% was reported from autoclaved ores.

The ability of ammonia to cause health problems in the workplace and of copper to cause excessive thiosulfate degradation prompted Ji et al. (2003) to investigate a new lixivant system that consists only of oxygen and sodium thiosulfate, without copper and ammonia. Experiments were performed on highly preg-robbing carbonaceous ore in an autoclave. The results showed 80% gold extraction at

60^{o}C, 10 psig to 100 psig oxygen pressure, and 0.1 M thiosulfate in 3 hours (C4 in Tables 2.6 and 2.7). Zhang et al. (2005) studied a new iron(III)/EDTA/thiosulfate-thiourea lixivant system using electrochemical and kinetic methods. The iron(III)-EDTA complex is an effective oxidant for the thiosulfate-thiourea leaching system, it has a low reactivity with thiosulfate due to complexation of Fe(III) with EDTA. Thiourea is a catalyst for gold oxidation. The addition of thiourea to the new lixivant system can significantly enhance the anodic oxidation of gold. The iron(III)/EDTA/thiosulfate-thiourea lixivant system can recover more than 90% gold from oxide ores (Zhang et al.,2005; O4 in Table 2.7).

2.4.4 Refractory ore

Ores that do not prove economical for gold recovery with conventional cyanidation are termed refractory (La Brooy et al., 1994). Perez and Galaviz (1987) patented a method for recovery of precious metals from refractory ores, such as an ore containing manganese and / or copper, using a copper-ammonia-thiosulfate solution. They claimed that the pH in leaching solutions should be maintained at about 9.5 in order to inhibit the decomposition of thiosulfate by iron(III) compounds. For mildly refractory ores (R1 in Table 2.6), Yen et al. (1998) conducted bottle-roll thiosulfate leach tests, which showed no indication of cupric ion and ammonia consumption. Thus, replenishing thiosulfate could allow recycling of the thiosulfate lixiviant. The gold extraction was 95% to 97% under the optimum leaching conditions described in Table 2.7 (R1), compared to the extraction of 80% to 90%

of gold in 24 hours with 0.5 g/l to 1.0 g/l NaCN. However, the reagent cost was 35% higher than that for cyanidation.

Zipperian et al. (1988) found that the leaching of fine-grained gold particles disseminated in a rhyolite ore (Rh in Table 2.6) was quite sensitive to thiosulfate and ammonia concentrations. Although copper(II) ions seemed to play a catalytic role, only 70% of gold was extracted at 50^{o}C when a very high thiosulfate concentration (about 3 M) was used. The authors highlighted the importance of maintaining E_H and pH to prevent precipitation of Cu_2S. Molleman and Dreisinger (2002) tested the leaching of a copper-gold concentrate and achieved a maximum of 84% gold extraction in 24 hours.

Xia and Yen (2005) conducted leaching experiments with pure silicate gold ores and noted that the presence of pyrite and pyrrhotite minerals led to lower gold recoveries and extraction rates, and largely increased the consumption of thiosulfate. A gold extraction of 93% was achieved in 3 hours, under the optimum leaching condition: 0.2 M thiosulfate, 0.9 M ammonia, 1.4 mM copper(II) and 0.3 ppm dissolved oxygen.

2.4.5 Pure gold

Many research groups have made valuable contributions to the understanding of the kinetics of gold oxidation in Cu(II)-NH_3-$S_2O_3^{2-}$ systems using massive gold in the form of foil or plates. Table 2.8 lists maximum gold dissolution rates obtained

by previous researchers. Feng and van Deventer (2002b) studied the dissolution behaviour of gold in ammoniacal thiosulfate systems, using gold foil of thickness 0.2 mm and surface area 0.2 cm^2. The results showed a gold dissolution of about 6 mg/cm^2, 10 mg/cm^2 and 20 mg/cm^2 in 3 hours, 5 hours and 10 hours respectively, at an average rate of 2.8 x 10^{-5} mol m^{-2} s^{-1}. However, much lower rates of 6 x 10^{-7} mol m^{-2} s^{-1} have been reported in solutions of low concentrations (Table, 2.8; Feng and van Deventer, 2007c).

Table 2.8 *Dissolution rates of gold under optimum conditions*

Gold type / Reference	T (^oC)	Oxygen	NH_3 (M)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	10^5 x Rate (mol m^{-2} s^{-1})
Gold disc / Breuer & Jeffrey (2000b)	30		0.4	5	0.1	4.2
Gold foil / Feng & van Deventer (2002b)	ambient	open to air	2	12	0.5	2.89
Gold foil / Feng & van Deventer (2007c)	25	N_2 or O_2	0.5	0.8	0.165[a]	0.058[b] 0.064[c]
Gold plates / Tozawa et al. (1981)	65	P_{O2} = 2 kg/m^2	1.0	80	0.48	9.6
Gold-silver alloy (5%Ag) / Jeffrey et al. (2001).	40		0.4	10	0.3	5.6
Gold / Jiang et al. (1993a)	50	open to air	4.4	310	1.0	90[d]

a. ammonium thiosulfate, pH 10; b. at nitrogen flow rate of 10 ml/min;
c. at oxygen flow rate of 10 ml/min; d. percentage dissolution.

Tozawa et al. (1981) used gold plates of dimension 14 x 15 mm and 1 mm thickness, and measured a gold dissolution rate three times higher than that reported by Feng and van Deventer (2002b) (Table 2.8). This indicated the beneficial effect of high temperature, oxygen pressure and copper concentration on gold dissolution. Bagdasaryan et al. (1983) used a rotating disc and conducted experiments in the temperature range 45°C to 85°C. The activation energy from their work (17.6 kJ/mol) was characteristic of a diffusion controlled reaction. They found deposits of sulfur and sulfides on the gold surface, and the rate determining factor in gold dissolution was believed to be the diffusion of ions through the sulfide layer.

Jeffrey et al. (2001a,b) compared the leaching of gold in cyanide and thiosulfate using a rotating electrochemical quartz crystal microbalance (REQCM) and reported leach rates in the range 2.1×10^{-5} mol m^{-2} s^{-1} to 5.6×10^{-5} mol m^{-2} s^{-1} in thiosulfate solution, comparable with those in cyanide (4.1×10^{-5} mol m^{-2} s^{-1}). Breuer & Jeffrey (2000b) also measured gold dissolution rates of the order 5.6×10^{-5} mol m^{-2} s^{-1}, which is much lower than a calculated copper(II) diffusion limited rate of 24.6×10^{-5} mol m^{-2} s^{-1}. This led to the conclusion that the leaching rate of gold was chemically controlled, which was supported by the reaction activation energy of 60 ± 10 kJ/mol.

Thus, the dissolution of gold under these experimental conditions is controlled by a slow surface reaction. It is important to consider the effect of concentration of

the main reagents on the rate of surface reaction during thiosulfate leaching of gold ores or massive gold.

2.5 Factors affecting the leaching of gold

2.5.1 Effect of thiosulfate concentration

The results obtained with gold plates, gold foil, or gold discs listed in Table 2.9a show the beneficial effects of increasing thiosulfate concentration on the rate of gold oxidation. Breuer and Jeffrey (2000b) and Jeffrey (2001) reported that an increase in thiosulfate concentration increased the rate of gold leaching (Table 2.9a). They proposed that at low concentrations of copper(II) and thiosulfate the leaching reaction was chemically controlled. At high concentrations of thiosulfate the reaction was controlled by the diffusion of copper(II). Feng and van Deventer (2002b) showed similar results on gold foil dissolution (Table 2.9a), where anodic and cathodic half reactions were enhanced by increasing thiosulfate concentrations. Results from experiments using gold plates at low oxygen pressures (Tozawa et al., 1981) showed that the gold dissolution rate increased with increasing thiosulfate concentration up to 0.44 M. At higher concentrations there was no appreciable effect on the dissolution rate. Selected literature data on the effect of increasing thiosulfate concentration on gold extraction from different types of ores are listed in Tables 2.9b, 2.9c.

Gold extraction of 10% to 20% has been achieved in copper(II)-ammonia solutions in the absence of thiosulfate (Zipperian et al., 1988; Cao et al., 1992; Chai, 1997; Ji and Yu, 1991). This was increased at higher temperatures and oxygen pressures, indicating the formation of $Au(NH_3)_2^+$ in the absence of thiosulfate (Han, 2001). A refractory copper-gold sulfide concentrate underwent self-catalysed leaching of gold due to the presence of copper(II) in ore (G4), but the recovery of gold increased from 6% to 80% when thiosulfate was increased from 0.24 M to 1.2 M (Jiang et al., 1992). Yen et al. (1998) used ammonia-thiosulfate solution to extract gold from a mildly refractory ore, and found that a decrease in thiosulfate concentration can dramatically decrease gold extraction efficiency, due to the higher ratio of $[NH_3]$ / $[S_2O_3^{2-}]$. However, ammonium thiosulfate concentrations higher than 0.5 M caused only a slight increase in gold extraction (Refractory ore in Table 2.9c).

Table 2.9a *Effect of thiosulfate concentration on gold dissolution rates*

Gold type / Reference	T (^oC)	NH_3 (M)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	10^5 X R (mol m^{-2} s^{-1})	Note
Gold disc / Breuer & Jeffrey (2000b)	30	0.4	0.005	0.05 0.2	1.1 8	a
Gold foil / Feng & van Deventer (2002b)	ambient	2	0.012	0.1[b] 0.5	2.8 29	c
Gold powder / Tozawa et al. (1981)	65	1.0	0.04	0.1 0.53	0.55 4.6	d

a. Nitrogen or Argon atmosphere;

b. $(NH_4)_2S_2O_3$;

c. Air or Oxygen atmosphere;

d. SO_2 atmosphere.

In the case of oxide ores (Table 2.9b), a higher thiosulfate concentration was beneficial for gold extraction, but the presence of a high concentration of sodium chloride has detrimental effects at high thiosulfate concentrations (Li and Kuang 1998, in Table 2.9b). A higher thiosulfate concentration is also detrimental to gold extraction from sulfide ores (Block-Bolten et al. 1985, in Table 2.9b), unless a high ammonia concentration (≥ 3 M) is maintained (Aylmore 2001; Bhaduri 1987; Cao et al. 1992, in Table 2.9b). In most other cases described in Table 2.9c, a higher thiosulfate concentration was beneficial for gold extraction in the presence or absence of ammonia. However, the extraction efficiency will decrease or become independent of thiosulfate at high concentrations. In the case of carbonaceous ore, gold extraction efficiency appeared less sensitive to thiosulfate concentration.

Table 2.9b *Effect of thiosulfate concentration on gold leaching*

Ore Type / Reference	T (^oC)	NH_3 (M)	SO_3^{2-} (mM)	Retention Time (hr)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	Au Recovery %
Gold plates Jiang et al. (1993a)	50			-	0.07	0.36 1.33	28 56
Oxidized ore Langhans et al. (1991)	Ambient	0.09	6.25	4[b]	1	0.05 0.125 0.2	25 30 38
Oxidized ore Ji & Yu (1991)	60	1.68	79	2	78	0.063 0.32 0.65 1	42 58 94 95
Oxidized ore Li and Kuang (1998)	50	1.5	0*	3[d]	-	0.5 0.8 1.0	84 96 84
Sulfide ore Block-Bolten et al. (1985)	21	1	-	2		0.125 0.5	60 25
Sulfide ore Block-Bolten et al. (1985)	63	1	-	2		0.125 0.5	63 38
Sulfide ore Aylmore (2001)	Ambient	4	-	48[c]	50	0.1 0.8	3 90
Sulfide ore Aylmore (2001)	Ambient	4	-	2[c]	50	0.1 0.8	12 42
Sulfide ore Bhaduri (1987)	35	3.0	90	1[d]	40	0.04 0.19	35 42
Sulfide concentration Cao et al. (1992)	60	3		2[d]	47	0.0[h] 0.1 0.2	20 80 97.7

Unless stated otherwise, atmosphere was not specified for reactions.

b. Nitrogen or Argon; c: SO_2; d: Air or Oxygen;

h. $(NH_4)_2S_2O_3$.

* Contained 1M NaCl.

Table 2.9c *Effect of thiosulfate concentration on gold leaching (continued)*

Ore Type / Reference	T (^oC)	NH_3 (M)	SO_3^{2-} (mM)	Re* (hr)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	Au Recovery %
Carbonaceous ore Hemmati (1987)	35	3.0	100	2[d]	50	0.088[h] 0.88	64 74
Carbonaceous ore Ji et al. (2003)	60	0	-	2[d]	0	0.05 0.1 0.2	65 72 73
Refractory ore Yen et al.(1998)	Ambient	6		10	100	0.1[h] 0.5 1.0	27 86 89
Chalcopyrite ore Navarro et al. (2002)	Ambient	1	-	7	50	0.1[h] 0.3 0.7	66 90 90
Rhyolite ore Zipperian et al. (1988)	50	4.1	-	2	234	0 0.06[h] 0.63 1.39	10 40 82 84
Silicate ore Xia and Yen (2005)	Ambient	0.9		3	4.7	0.067 0.27 2.7	78 89 78
Gold (bearing) ore Chai (1997)	25	2		3[b]	1000 120	0 0.1[h] 0.29 0.57	10 46 72 68
Gold (bearing) ore Abbruzzes et al. (1995)	Ambient	4		3	0.1	0.125 2.0	15 80
Gold (bearing) ore Jiang et al. (1992)	Ambient	1.47		4		0.24 1.20	6 80

Unless stated otherwise, atmosphere was not specified.

b. Nitrogen or Argon;

d. Air or Oxygen;

h. $(NH_4)_2S_2O_3$.

*Re. Retention Time.

2.5.2 Effect of copper concentration

Jeffrey (2001) investigated the relationship between reaction rate and copper(II) concentration (< 5 mM) at 30^{o}C when thiosulfate and ammonia concentrations were maintained at 0.4 M and 0.84 M respectively. The linear increase in extraction rate with increasing copper(II) concentration was related to the diffusion of copper(II) ions to the gold surface. Above 5 mM copper(II), however, the rate became almost independent of the concentration of copper(II). Jiang et al. (1993a) studied the dissolution kinetics of gold by measuring the loss of mass from a gold plate in ammoniacal thiosulfate solution. Their results showed that the concentration of $Cu(NH_3)_4^{2+}$ had a dramatic effect on the dissolution rate of gold. Over the concentration range of 1 mM to 100 mM, the increase in rate was proportional to the concentration of $Cu(NH_3)_4^{2+}$ ion. The gold extraction from gold plates also increased from 20% to 90% with an increase in copper(II) concentration from 0% to 2% (Jiang et al., 1993a,b).

In the absence of copper(II), the aerated thiosulfate leaching of gold is very slow. The presence of copper(II) ion in thiosulfate-ammonia solution can increase the rate of gold dissolution by 18 - 20 fold (Aylmore & Muir, 2001a). Table 2.10 summarizes the effect of copper(II) concentration on the percentage of gold extracted from different types of materials. Despite the reaction between copper(II) and thiosulfate, the increase in copper(II) concentration has a positive effect on gold extraction.

As noted in Table 2.7, the optimum copper(II) concentration depends on the type of ore and concentrations of other reagents. These observations also suggest the possible participation of copper(II) in the chemical breakdown of host minerals.

Table 2.10 *Effect of copper concentration on gold leaching*

Ore type / Reference	T(°C)	NH_3 (M)	Na_2SO_3 (mM)	Retention Time (hr)	$Na_2S_2O_3$ (M)	Cu(II) (mM)	Au Recovery %
Gold disc Jeffrey et al. (2001b)	30	0.84		-	0.4[h]	0 1 5 25	0 1.6[k] 6.2[k] 10[k]
Gold powder Jiang et al. (1993a)	50	7.5%		-	1.0	0 62.5 312	20 56 90
Refractory ore Ji & Yu (1991)	60	1.7	79	2	0.63	2 20 40	38 94 95
Refractory Sulfide ore Aylmore (2001)	Ambient	4		24[c]	0.8	12.5 50 62.5	20 90 70
Refractory Au-Cu ore Yen et al. (1998)	Ambient	6M		10	0.5[h]	30 200	70 87
Rhyolite ore Zipperian et al. (1988)	50	4.1		1	1.4[h]	23 940	83 88
Carbonaceous Ore West-Sells and Hackl (2005)	Ambient	0.2		24[d]	0.1	5 50 100	64 75 78
Silicate ore Xia & Yen (2005)	Ambient	0.9		3	0.2	4.7 15.7 47	84 92 92
Gold ore Abbruzzese et al. (1995)	25	4		2	2	30 100	30 80
Gold concentrate Navarro et al. (2002)	Ambient	0.5		7	0.3[h]	10 50 100	80 90 82

Unless stated otherwise, atmosphere was not specified;

k. Rate x 10^5 (mol m^{-2} s^{-1}); c. SO_2; d. Air or Oxygen; h: $(NH_4)_2S_2O_3$.

2.5.3 Effect of ammonia concentration

Tozawa et al. (1981) conducted autoclaved leaching experiments (Table 2.11) and reported that the maximum dissolution rate of gold plate was observed in 0.5 M ammonia. The decrease in dissolution rate, at ammonia concentrations higher than 0.5 M, was related to an increase in OH^- ions, which suppress the dissolution of gold. Breuer & Jeffrey (2000a,b) found that the reaction rate decreased in the ratio of 3:2:1, with increasing concentration of ammonia in the ratio 0.2 M : 0.4 M : 0.6 M (Table 2.11). The decrease in dissolution rate was related to the fact that the mixed potential became more negative with the increase in ammonia concentration. For example, the enhanced stability of copper (II), according to Eq. 2.49, reduced the reduction potential of the cathodic half-cell reaction:

$$Cu(NH_3)_4^{2+} + 3(S_2O_3)^{2-} + e = Cu(S_2O_3)_3^{5-} + 4NH_3 \qquad (2.49)$$

Tozawa et al. (1987) believe that there is an optimum ammonia concentration at which a maximum leaching rate is observed. If the concentration of ammonia is lower than this value, excess copper(II) reacts with thiosulfate to reduce the concentration of cupric tetra ammine available for the oxidation of gold. If the concentration of ammonia is greater than the optimum value, it will decrease the reduction potential of the copper(II)/copper(I) couple, thereby decreasing the oxidising ability of copper(II). The optimum ammonia concentration is dependent on thiosulfate and copper concentrations. Feng and van Deventer (2002a,b) also

observed the negative effect of concentrated ammonia in a set of electrochemical experiments that used 0.1M $Na_2S_2O_3$ and 0.5 M to 2.0 M NH_3 (Table 2.11).

Without ammonia, thiosulfate can leach only 0% to 4% gold from a sulfide ore (Cao et al., 1992) and 32% gold from a gold concentrate containing copper (Jiang et al., 1992). Although the main role of ammonia is to stabilise cupric ions by forming copper(II)-ammine complexes, it also prevents the formation of elemental sulfur on the surface of gold (Chen et al., 1996). Most of the published data (Table 2.11) show that an increase in ammonia concentration has a positive effect on gold extraction up to a point, but very high ammonia concentration has little benefit or may exert a negative effect on gold extraction (Yen et al., 1998; Chai, 1997; Gong et al., 1993).

Aylmore (2001) reported results for a refractory gold-copper sulfide concentrate (Table 2.11) where the gold extraction increased from 80% to 95% as the ammonia concentration was increased from 1.5 M to 4 M. In contrast, Chai (1997) reported that from a range of ammonia concentrations of 0 M to 6 M, the highest gold extraction of 90% was achieved in a solution of 2 M ammonia, 0.12 M copper(II), and 0.287 M thiosulfate at 60°C in 3 hours. Yen et al. (1998) obtained results similar to those of Aylmore (2001) from a mildly refractory gold-copper ore from Canada. Gold recovery increased from 60% to 85% as ammonia concentration was increased from 1 M to 6 M. However, a further increase in ammonia to 9 M

reduced the gold extraction to 5%. Their explanation for these observations was based on the equilibrium between the two gold(I) complexes:

$$Au(NH_3)_2^+ + 2(S_2O_3)^{2-} = Au(S_2O_3)_2^{3-} + 2NH_3 \quad (2.50)$$

A high concentration of ammonia makes the equilibrium favourable to the left, therefore reducing the gold extraction (Yen et al., 1998).

Abbruzzese et al. (1995) noted that the rate of gold dissolution from a gold-bearing ore was rapid during the first hour. Gold recovery increased from 50% to 78% and then decreased to 2% as the concentration of ammonia was changed from 1 M to 4 M and then to 8 M (Table 2.11). They concluded that the increase in ammonia concentration reduced the thermodynamic stability of $Cu(NH_3)_4^{2+}$ and $Cu(S_2O_3)_3^{5-}$, widening the regions of thermodynamic stability of CuO and Cu_2O. They noted that the precipitation of CuO reduced the activity of the $Cu(NH_3)_4^{2+}$ complex and hindered the thiosulfate attack by covering the mineral surface. It can be seen from the E_H-pH diagram in Fig. 2.1a and Fig. 2.3 (Aylmore and Muir, 2001) that the rise in pH caused by the increase in ammonia enlarges the stability area of CuO and Cu_2O. In general, an increase in ammonia concentration increases gold extraction. The most effective ammonia concentration is in the range 0.5 M to 6 M, while the most appropriate ratio of $[NH_3]$ / $[Na_2S_2O_3]$ is 0.3 to 6 depending on the type of ore.

Table 2.11 *Effect of ammonia concentration on gold leaching*

Ore type / Reference	T (^oC)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	NH_3 (M)	Retention Time (hr.)	Au Recovery %
Gold disc Jeffrey et al. (2001a,b)	30	0.025	0.4[h]	0.4 1.68		11.9[k] 6.3
Gold disc Breuer & Jeffrey (2000b)	30	0.01	0.1	0.2 0.6	-[b]	6.0[k] 2.0
Gold powder Tozawa (1981)	65	0.04	0.25	0 0.5 3.0	3[d]	0 g/m^2 150 g/m^2 50 g/m^2
Gold foil Feng & van Deventer (2002a,b)	Ambient	0.012	0.1[h]	0.5 2.0	24[d]	90 50
Oxidized ore Ji & Yu (1991)	60	78	0.63	0.82 1.71 5.2	2	80 94 95
Oxidized Ore Li & Kuang (1998)	50	-	0.8	0.1 0.5 1	2[d]	74 96 94
Sulfide ore Aylmore (2001)	Ambient	50	0.8	1.5 3 4	24[c]	60 75 75
Refractory ore Yen et al. (1998)	Ambient	100	0.5[h]	1 6 9	24	80 96 90
Rhyolite ore Zipperian et al. (1988)	50	230	1.4[h]	0.41 8.2	1	83 86
Silicate ore Xia &Yen (2005)	Ambient	4.7	3	0.2	0.2 2.7	78 94
Gold concentrated Jiang et al. (1992)	Ambient		1.3	0 7.35	3-4	32 94
Gold ore Jiang et al. (1992)	25	0.1	2	1-4 4-8	3	50-78 78-2

Unless stated otherwise, atmosphere was not specified.

b. Nitrogen or Argon;

c. SO_2;

d. Air or Oxygen;

k. Rate x 10^5 (mol m^{-2} s^{-1});

h. $(NH_4)_2S_2O_3$;

i. Contained 1% Na_2SO_3.

2.5.4 Effect of pH

At a given temperature, the total concentration of $NH_3 + NH_4^+$, pH and pK_a (= -log K_a) govern the concentration of NH_3:

$NH_4^+ = NH_3 + H^+$ (K_a = equilibrium constant) (2.51)

$[NH_3] = [NH_3 + NH_4^+] / \{10^{(pKa-pH)} + 1\}$ (2.52)

Most laboratory (batch) leaching tests reported in the literature have been conducted in the pH range of 9.5 - 10.5. This is due to the fact that at pH values lower than 9, gold extraction is retarded due to the low concentration of free ammonia and the precipitation of CuO. At pH values higher than 10.5, the precipitation of Cu_2S, CuO or Cu_2O (E_H-pH diagram in Fig. 2.1) retards gold extraction. Thus, maximum recovery of gold can be obtained in the pH range 9.5 - 10.5, as shown in Table 2.12.

At low pH values and low total ammonia, the rate of gold dissolution increased with increasing pH values, due to the increase in the stability of copper(II) caused by high ammonia concentration. When pH values were changed from 9.8 to 11.4, the rate decreased from 6 $x10^{-5}$ mol m^{-2} s^{-1} to 4 x 10^{-5} mol m^{-2} s^{-1} (Breuer and Jeffrey, 2000a,b). Similar results were obtained from experiments using gold plates (Jiang et al., 1993a), where a change in pH value from 8 to 10 increased gold dissolution from 30% to 55%, but a further increase in pH value to 11 decreased gold dissolution to 50% (Table 2.12). The decrease in rate at high pH values is similar to the effect of high concentration of ammonia observed in Table 2.11.

Table 2.12 *Effect of pH on gold leaching*

Ore Type / References	T (ºC)	NH_3 (M)	Retention Time (hr.)	Cu(II) (mM)	$S_2O_3^{2-}$ (M)	pH	Au Recovery %
Gold disc Breuer & Jeffrey (2000b)	30	0.4	-[b]	0.005	0.1	9.8 10.8 11.4	6[k] 4.8[k] 4[k]
Gold plates Jiang et al. (1993a)	50		-	0.0625	1.0	8 10 11	30 55 50
Carbonaceous [n] Hemmati (1987)	55	up to 4.5	2[d]	60	1.19[h]	9 10.5	8 60
Carbonaceous West-Sells & Hackl (2005)	Ambient	0.2	24[d]	0.79	0.1	8 9 9.5 10	70 75 73 64
Refractory Yen et al. (1998)	Ambient	6	10	100	0.5[h]	8.5 10 11.5	10 85 50
Chalcopyrite Navarro et al. (2002)	Ambient		15	50	0.7[h]	9 10	10 92
Gold bearing [p] Chai (1997)	60	0.29-2.3	2.5[b]	120	0.287[h]	8.5 10.5 11	72 89 87.5

Unless stated otherwise, atmosphere was not specified for reactions.

b. Nitrogen or Argon; d: Air or Oxygen;

k. Rate x 10^5 mol m^{-2} s^{-1};

h. $(NH_4)_2S_2O_3$;

n. 220 mM SO_3^{2-};

p. 0.8 M SO_4^{2-}.

2.5.5 Effect of temperature

It is notable that the results from experiments that used pure gold (Table 2.13) showed a positive effect with increase in temperature from 25ºC to 40ºC (Breuer and Jeffrey 2000a,b). Experiments with gold plates (Tozawa et al., 1981) under an

oxygen pressure in the range of 0.2 kg/cm^2 to 10 kg/cm^2 showed a positive effect in the temperature ranges 18°C to 60°C and 100°C to 140°C. In contrast, a negative effect was shown in the temperature range 60ºC to 100ºC and 140ºC to 180ºC (Table 2.13). The decrease in rate of gold dissolution from 65°C to 100°C has been related to the formation of cupric sulfide on the gold surface. However, at temperatures below 140^{o}C, the rate showed a remarkable increase as a result of thiosulfate ions being regenerated on the surface of gold by the oxidation of cupric sulfide (Tozawa et al., 1981). The increase in temperature from 140ºC to 180ºC caused a decrease in dissolution rates of gold due to the enhanced oxidation of thiosulfate ions.

Table 2.13 also summarizes the effect of increase in temperature in the range 25°C to 80°C on gold extraction from different types of gold ores. Most of the previous studies indicate that the increase in temperature from 25ºC to 50ºC or 60ºC has a positive effect, which in turn could lead to a 10% to 50% increase in gold extraction (Zipperian et al., 1988; Ji and Yu, 1991; Cao et al., 1992; Chai, 1997; Li and Kuang, 1998; Zhang and Li, 1987). Some other important aspects are as follows:

(i) Results from an oxide gold ore showed that gold extraction increased from 74% to 100% as the temperature was increased from 30ºC to 50ºC, and decreased to 95% with a further increase in temperature to 60ºC in 3 hours (Li and Kuang, 1998).

(ii) Results from a Rhyolite ore (Zipperian et al., 1988) showed that almost 90% of gold was solubilized in one hour at 60ºC, compared to only 25% of gold solubilized at 25ºC.

(iii) Results from a refractory gold ore in the temperature range 30ºC to 55ºC (Ji and Yu, 1991) showed that the gold recovery increased from 6% at 30ºC to 89% at 55ºC, but a further increase in the leaching temperature to 65ºC had little effect on gold recovery.

(iv) Similar results were obtained from a sulfide copper-gold concentrate (Cao et al., 1992) in which gold was found to be predominantly associated with pyrite, chalcopyrite and bornite. The gold extraction increased from 52% (30°C) to 89% (40ºC) and to 97.7% (60ºC), no further increase in extraction was observed beyond 60ºC.

(v) Chai (1997) reported that the change in temperature from 25ºC to 80ºC only slightly affected the extraction of gold, which led to the conclusion that diffusion and transport processes are likely to be the rate-limiting step.

(vi) Abbruzzese et al. (1995) reported a negative effect of high temperature on gold extraction, where a decrease from 79% to 56% was observed when the temperature was increased from 25ºC to 60ºC. They also related this behaviour to the passivating effect of cupric sulfide formed and the decomposition of thiosulfate to sulfur compounds according to Eqs. 2.29 - 2.31:

$$Cu(II) + S_2O_3^{2-} + 2OH^- \rightarrow CuS + SO_4^{2-} + H_2O \qquad (2.29)$$

$$2S_2O_3^{2-} + H_2O + 0.5O_2 = S_4O_6^{2-} + 2OH^- \quad (2.30)$$

$$3S_2O_3^{2-} + 3H_2O = 4SO_3^{2-} + 2S^{2-} + 6H^+ \quad (2.31)$$

Thus, the effect of temperature on gold extraction is largely dependent on the composition (mineralogy) of gold ore which may lead to the precipitation of various solids on the gold surface, especially at high temperatures. The general trend within a low temperature range of 25ºC to 60ºC is a positive effect with increasing temperature.

Table 2.13 *Effect of temperature on gold leaching*

Gold / Ore type / Reference	NH_3 (M)	Retention time (hr.)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	T(^oC)	Au Recovery % or Rate
Gold disc Breuer & Jeffrey (2000b)	0.4	-[b]	0.01	0.1	25 30 40	Reaction rate increases significantly
Gold plates Tozawa et al. (1981)	0.5	3[d]	0.04	0.25	20 60 100 140 180	(20) (120) (20) (140) (60)
Oxide ore Li and Kuang (1998)	1.5[m]	2[d]	-	1	30 50 60	70 95 95
Sulfide gold Concentrate Cao et al. (1992)	3	2[d]	47	0.2[h]	30 50 60	52 94 97
Refractory ore Ji & Yu (1991)	1.7[n]	2	78	0.63	30 50 60	66 88 89
Rhyolite Zipperian et al. (1988)	4.1	3	230	1.4[h]	25 50 60	70 90 90
Gold ore Abbruzzese et al. (1995)	4	3	100	2	25 40 60	79 75 56
Gold-bearing ore Chai (1997)	2	3[b]	120	0.287[h]	20 60 80	80 90 75

Unless stated otherwise, atmosphere was not specified for reactions; values in parentheses show rates in (g/m^2).

b: Nitrogen or Argon;

d: Air or Oxygen;

h: $(NH_4)_2S_2O_3$;

m: 1 M NaCl; n: 79 mM Na_2SO_3.

2.5.6 Effect of sulfur containing anions

Chu et al. (2003) studied the impact of thiosulfate oxidation products on the oxidation of gold in ammoniacal thiosulfate solutions. They found that the addition of sulfur-oxy species, which could be produced by the oxidation of thiosulfate, could decrease the oxidation rate of gold as shown in Table 2.14. Experiments were carried out at a constant potential of 250 mV and oxygen-sparging rate of 200 ml/minute. The disulfite ion ($S_2O_5^{2-}$) gave the largest negative impact on the oxidation of gold. Thus, it was postulated that disulfite, which is an intermediate product of thiosulfate oxidation by copper(II) in the presence of oxygen (Byerley et al., 1975), was responsible for the slow leaching kinetics. The gold dissolution from a sulfide ore increased with the addition of sulfur species such as tetrathionate, trithionate and sulfide at low levels, but decreased at high levels (Feng and van Deventer, 2007a).

Table 2.14 *Effect of sulfur-oxy species on gold dissolution rates*

Sulfur-oxy species	No addition	$S_4O_6^{2-}$ (25 mM)	SO_4^{2-} (25 mM)	$S_3O_6^{2-}$ (25 mM)	$S_2O_5^{2-}$ (25 mM)
10^5 R/(mol m^{-2} s^{-1})	3.25	2.75	2.85	2.9	0.25

Addition of sulfite can inhibit the precipitation of sulfur and copper sulfide as noted in Section 2.3.5 (Eqs. 2.35 - 2.36). Some researchers have reported that sulfite and sulfate ions can stabilize thiosulfate in solutions (Section 2.3.5) and thus be

beneficial in gold leaching (Zhang and Li, 1987). However, the addition of sulfite would decrease E_H, so this effect could be positive, negative or negligible. Some examples of the different observed effects of sulfite and sulfate addition are as follows:

(i) Zhang and Li (1987) found that the effect of sulfite on gold extraction from a concentrate was dependent on the ratio of $[S_2O_3^{2-}]$ / $[SO_3^{2-}]$. They added sulfite to ammoniacal thiosulfate solution to stabilize thiosulfate and found that a ratio of $[S_2O_3^{2-}]$ / $[SO_3^{2-}]$ = 4 gave the highest extraction of gold (95%) and silver from gold concentrates.

(ii) Bagdasaryan et al. (1983) studied the dissolution rate of gold and silver using a rotating disc. They found that the addition of sodium sulfite to thiosulfate solution prevented the deposition of sulfur and sulfides on the surface of the gold and silver disc. The optimum molar ratio of sodium sulfite to sodium thiosulfate for this effect was 1:1.

(iii) Electrochemical studies by Sullivan and Kohl (1997) have showed that the reduction peak of gold thiosulfate shifted in the negative direction with increasing sulfite concentration. This may have been due to the formation of a mixed Au(I) complex of thiosulfate and sulfite, or sulfite adsorbed onto the gold substrate. Recent studies have confirmed the formation of mixed Au(I)-$S_2O_3^{2-}$-SO_3^{2-} complexes (Perera et al., 2005).

(iv) Gold extraction increased from 30% to 42% in leaching experiments on a refractory ore in the presence of sulfite up to 0.09 M (Bhaduri, 1987).

(v) Sulfite concentration up to 0.4 M at 55ºC gave a positive effect in experiments conducted with carbonaceous ore, but the addition of up to 0.4 M sulfite at a lower temperature of 35ºC showed no effect (Hemmati, 1987).

(vi) The leaching of a flotation concentrate gave similar results (Navarro et al., 2002), where the addition of 0.07 M sulfite slightly increased the gold dissolution from 71% to 74%.

(vii) Sulfate addition has also shown a positive effect with up to 9% increase in gold extraction (Chai, 1997).

(viii) Xia et al. (2002) showed that the addition of sulfite, sulfide and sulfate had beneficial effects on gold extraction.

(ix) The addition of 6.25 mM sulfite showed a negative effect on gold leaching from an oxide ore (Langhans et al., 1992), while the addition of 12.5 mM sulfite showed a negligible effect on gold extraction from a sulfide concentrate (Navarro et al., 2002).

(x) Wan (1997) investigated gold leaching from carbonaceous-sulfide ore, but did not find a beneficial effect caused by the addition of sulfite in a heap leach operation system. He suggested that an excess of sulfite may significantly change the redox potential of the system and affect gold extraction.

(xi) Ji and Yu (1991) claimed that the addition of sodium sulfite did not reduce the consumption of thiosulfate during the leaching of refractory gold ore using thiosulfate.

(xii) The leaching results of sulfide ore in a copper(II)-ammonia-thiosulfate system (Feng and van Deventer, 2002a,b) showed that the presence of sulfides in the leaching system enhanced the decomposition of thiosulfate.

In summary, there is no clear understanding on the role of sulfur containing anions in the leaching and recovery of gold using the Cu(II)-NH_3-$S_2O_3^{2-}$ system, warranting further studies.

2.5.7 Effect of retention time

The effect of retention time on gold extraction is dependent on leaching conditions, where increased leach time is more beneficial at low thiosulfate concentration than at high thiosulfate concentration. These effects are summarised in Table 2.15. In general, the increase in retention time increases gold dissolution, but longer retention times are not necessarily effective in some cases. It is clear from Table 2.15 that in the case of carbonaceous or sulfide ores at temperature 50ºC to 60ºC and thiosulfate concentration 0.6 M to 1 M, gold extraction in the first hour can be as high as 70% to 90% due to the faster leaching rate. However, a further increase in leaching time showed no significant influence on gold extraction. In other cases, low temperature or low reagent concentrations caused low leaching rates, and longer residence time benefited gold extraction. For example, in the case of an oxidized ore noted in Table 2.15, increase in residence time from 4 hours to 48 hours improved gold recovery from 32% to 82% at ambient conditions (Langhans et al., 1992). For the second oxidized ore in Table 2.15, gold recovery increased from 51% to 74% as the residence time was increased from 0.5 hour to 3 hours at 30^{o}C (Li and Kuang, 1998). Chalcopyrite, a gold concentrate, and a refractory ore showed similar trends (Table 2.15).

Table 2.15 *Effect of retention time on gold leaching*

Ore Type / Reference	T (^oC)	NH_3 (M)	Cu(II) (mM)	$Na_2S_2O_3$ (M)	Retention Time (hr.)	Au Recovery % or rates
Pure gold Jiang et al. (1993a)	50		0.063	0.95	1 4	50 52
Gold foil Feng & van Deventer (2002b)	Ambient	2	0.012	0.5 [h]	5[d] 24	100 g/m^2 500 g/m^2
Oxide ore Langhans et al. (1992)	Ambient	0.09[m]	1	0.125	4[b] 48	32 82
Oxide ore Li & Kuang (1998)	30	1.5[n]	-	1	0.5[d] 3	51 74
Carbonaceous Hemmati (1987)	55	3.0[s]	150	0.71 [h]	1[d] 4	70 72
Carbonaceous Wan & Brierley (1997)	Ambient	0.1	0.5	0.1	60 days	62
Chalcopyrite Navarro et al. (2002)	Ambient	1	50	0.3 [h]	1 10	40 90
Rhyolite Zipperian et al. (1988)	50	4	230	0.63 [h]	1 3	80 85
Refractory Bhaduri (1987)	60	3.0[p]	64	1.35 [h]	0.5[d] 2.5	68 75
Refractory Yen et al., 1998	Ambient	6	100	0.25 [h]	10 24	50 80
Sulfide Block-Bolten et al. (1985)	21	1	-	0.125	1 3	60 61
Sulfide ore Gong & Hu (1990)	50	2	160	1	1[d] 2	92 94.5
Sulfide concentrate Cao et al. (1992)	60	3[q]	47	0.2 [h]	1[d] 3	97.4 93.5
Sulfide ore Aylmore (2001)	Ambient	3[r]	50	0.8	2[c] 24	40 75
Gold-bearing ore Chai (1997)	25	2[q]	120	0.287[h]	1[b] 3	55 70
Gold ore Abbruzzes et al. (1995)	25	4	100	2	1 3	68 80
Gold concentrate Ji et al. (2003)	Ambient		50	0.3[h]	0.5 7	32 90

Unless stated otherwise, atmosphere was not specified.

b. Nitrogen or Argon; c. SO_2; d. Air or Oxygen;

h. $(NH_4)_2S_2O_3$.

m. 6.3 mM Na_2SO_3; n: 1 M NaCl;

p. 110 mM Na_2SO_3; q. 0.8 M Na_2SO_4;

r. SO_2 gas; s. 100 mM Na_2SO_3.

2.5.8 Effect of foreign ions

Feng & van Deventer (2002b) studied how heavy metal ions would affect gold dissolution kinetics. They used gold foils (99.99% Au) and found that the presence of lead at a low concentration (50 mg/l) increased gold dissolution, but a high concentration inhibited it. Metals such as cadmium, nickel, cobalt and chromium inhibited gold dissolution at all reagent concentrations, but zinc had a slightly positive effect at very low concentrations (10 mg/l). At zinc(II) concentrations higher than 10 mg/l, the rate of gold dissolution and the free thiosulfate concentration decreased. This was related to the decomposition of thiosulfate or the formation of thiosulfate complexes with foreign metal ions.

Results based on a sulfide concentrate (Navarro et al., 2002) showed that the addition of 4.5 g/l zinc(II) to thiosulfate solutions reduced gold extraction from 92% to 86% after 10 hours. Chai (1997) showed that the addition of zinc(II) reduced thiosulfate concentration by forming complex species such as $Zn(S_2O_3)_n^{2-2n}$. Webster (1986) found that the presence of silver-thiosulfate complexes or alloyed silver increased the rate of gold dissolution in oxygenated 0.1 M thiosulfate solution.

Li and Kuang (1998) reported that NaCl could increase gold extraction from an oxide ore. For example, the addition of 1 M NaCl enhanced gold extraction from

39.3% to 84% in ammonium thiosulfate solution. They noted that chloride increased gold dissolution according to the reaction:

$$2Au + 4Cl^- + 0.5O_2 + H_2O = 2AuCl_2^- + 2OH^- \quad (2.55)$$

where the intermediate $AuCl_2^-$ ($\beta_2 \approx 10^9$) is subsequently converted to the more stable thiosulfate complex: $Au(S_2O_3)_2^{3-}$ ($\beta_2 \approx 10^{26}$, Table 1.2).

$$AuCl_2^- + 2(S_2O_3)^{2-} = Au(S_2O_3)_2^{3-} + 2Cl^- \quad (2.56)$$

The formation of $AuCl_2^-$ reduces the reaction activation energy, which in turn increases the reaction rate (Li and Kuang, 1998). However, the half reaction for gold oxidation in Eq. 2.55 seems unlikely as Eh required for the oxidation of Au to $AuCl_2^-$ is too high compared to that of Cu(II)/Cu(I)-ammonia-thiosulfate system.

2.5.9 Effect of oxidants

Gold dissolution in the ammonia-thiosulfate system is caused by copper (II) acting as the oxidant. The direct oxidation of gold by oxygen in thiosulfate media is very slow as revealed by the results reported by Chai (1997) from a gold-bearing ore using oxygen or copper(II), or both of them as oxidants (Table 2.16).

Table 2.16. *Effect of oxidants on gold leaching*

Oxidant	Air bubbling	Open to air	Cu(II)/N_2	Cu(II)/open to air	Cu(II)/air bubbling
Au recovery % after 3 hours	28	32	52	76	90

2M NH_3, 0.287 M to 0.8 M $(NH_4)_2SO_4$, temperature: 25ºC to 60ºC (Chai, 1997).

Air as an oxidant can only oxidize 28% to 32% of gold to gold(I) after 3 hours, whereas Cu(II) / N_2 can oxidize 52% and copper(II) / air bubbling can oxidize 90% of gold (Table 2.14). This has been attributed to the low solubility and hence low diffusion rate of oxygen, compared to $Cu(NH_3)_4^{2+}$. Although oxygen is a slower oxidant compared to copper(II), it can oxidize copper(I) to copper(II) and thus facilitate the leaching process (Ritchie et al., 2001):

$$Au + Cu(II) = Au(I) + Cu(I) \quad (2.57)$$

$$2Cu(I) + 0.5O_2 + H_2O = 2Cu(II) + 2OH^- \quad (2.58)$$

Han (2001) conducted electrochemical leaching experiments with various oxidants: 0.157 M $Cu(NH_3)_4^{2+}$, 0.047 M $Co(NH_3)_6^{3+}$, 1200 kPa O_2, and 0.32 M NaOCl. He found that the descending order of oxidation ability was:

(Cu(II) + NaOCl) > (Cu(II) + O_2) > Cu(II) > Co(III) > O_2 > NaOCl.

Breuer and Jeffrey (2002) obtained similar results in their electrochemical study of gold oxidation in thiosulfate solutions. For the three oxidants: copper(II), cobalt(III) and O_2 in 0.1 M $(NH_3)_2S_2O_3$ and 0.2 M NH_3, at the same mixed potential of 175 mV, the oxidation ability decreased in the order Cu(II) > Co(III) > O_2. A systematic study of speciation, reaction rates, and mechanisms is essential to understand the relative effects of oxidants and ligands on gold extraction. Gold colloids used in this work have larger surface area leading to fast reaction kinetics, even at low concentration of 0.1 mM Au(c). This allowed the use of relatively low concentrations of reagents compared to the previous work with ores and concentrates (Tables 2.8-2.15).

2.6 The mechanism of gold dissolution in a Cu(II)-NH_3-$S_2O_3^{2-}$ system

Despite a large number of research publications on fundamentals and leaching studies, the leaching chemistry and reaction mechanism for the oxidation of gold by copper(II) remains unclear. This complexity is largely due to a number of competing reactions within the system, such as the reduction of Cu(II) to Cu(I) by $S_2O_3^{2-}$ producing polythionates, and the subsequent oxidation of Cu(I) to Cu(II) by oxygen. Few attempts have been made to compare the results from fundamental studies with leaching results. Some interpretations presented by previous researchers are described below:

(i) Zhang and Li (1987) identified that the leaching process from a sulfide gold concentrate involved a diffusion (shrinking core) controlled reaction. The apparent activation energy for gold dissolution from ores was about 12 kJ/mol. Cathodic reaction of copper(II) to copper(I) and the oxidation of copper(I) to copper(II) were described by Eqs. 2.59 - 2.60:

$$Cu(NH_3)_4^{2+} + e^- = Cu(NH_3)_3^{+} + NH_3 \quad (2.59)$$

$$2Cu(NH_3)_3^{+} + 0.5O_2 + H_2O + 2NH_3 = 2Cu(NH_3)_4^{2+} + 2OH^- \quad (2.60)$$

(ii) Gong et al. (1993) claimed that the corrosion reaction of pyrite controls the kinetics of gold leaching in thiosulfate solution. This process consists of two stages. The initial stage (in the first 5 minutes) involves the dissolution of gold

and this includes free gold and gold exposed on the surface of granules of chalcopyrite. The second stage of the reaction is controlled by diffusion of reagents through solid reaction products. Copper(II) ions catalyse the initial dissolution of gold. These complex issues led to more fundamental work on the reaction mechanism of gold oxidation.

(iii) Jiang et al. (1993b) proposed the following mechanism of gold leaching with ammoniacal copper(II) in thiosulfate media (Eqs. 2.61 - 2.65):

$$Au = Au^{+} + e^{-} \quad \text{(Anodic process)} \tag{2.61}$$

$$Au^{+} + 2NH_3 = Au(NH_3)_2^{+} \tag{2.62}$$

$$Au(NH_3)_2^{+} + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + 2NH_3 \tag{2.63}$$

$$Cu(NH_3)_4^{2+} + e^{-} = Cu(NH_3)_2^{+} + 2NH_3 \quad \text{(Cathodic process)} \tag{2.64}$$

$$Cu(NH_3)_2^{+} + 0.25O_2 + 0.5H_2O + 2NH_3 = Cu(NH_3)_4^{2+} + OH^{-} \tag{2.65}$$

On the anodic gold surface, Au^{+} ions react with ammonia to form the complex $Au(NH_3)_2^{+}$. After entering the solution, $Au(NH_3)_2^{+}$ reacts with $S_2O_3^{2-}$ to form the more stable complex $Au(S_2O_3)_2^{3-}$. On the cathodic surface, $Cu(NH_3)_4^{2+}$ is reduced to $Cu(NH_3)_2^{+}$. After entering the solution, oxygen oxidises $Cu(NH_3)_2^{+}$ back to $Cu(NH_3)_4^{2+}$. Wensveen and Nicol (2005) showed that the oxidation of $Cu(NH_3)_2^{+}$ by oxygen (Eq. 2.65) is much faster than the oxidation of $Cu(S_2O_3)_2^{3-}$.

(iv) Zhu et al. (1994b) conducted an electrochemical study on the mechanism of gold dissolution in thiosulfate solutions. They reported that in the absence of ammonia, the anodic process of the gold electrode consists of an active dissolution reaction described by Eqs. 2.61 and 2.66.

$$Au \rightarrow Au^{+} + e^{-} \quad (2.61)$$

$$Au^{+} + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} \quad (2.66)$$

and a simultaneous passivation reaction occurs with the adsorption of elemental sulfur on the surface of the electrode (Eqs. 2.67 - 2.68):

$$S_2O_3^{2-} + Au \rightarrow Au\,|\,S^0 + SO_3^{2-} \quad (2.67)$$

$$S^{2-} + Au \rightarrow Au\,|\,S^0 + 2e \quad (2.68)$$

(iv) The addition of ammonia into the thiosulfate system can eliminate the passivation of the electrode as described in Eqs. 2.61, 2.62 and 2.63 proposed by Jiang et al. (1993b).

(v) Aylmore and Muir (2001a) proposed an electrochemical-catalytic mechanism in which gold ions react with thiosulfate ions to form $Au(S_2O_3)_2^{3-}$ after entering solution (Eq. 2.63). On the cathodic surface, $Cu(NH_3)_4^{2+}$ is reduced to $Cu(NH_3)_2^{+}$. After entering solution, oxygen oxidises $Cu(NH_3)_2^{+}$ back to $Cu(NH_3)_4^{2+}$ as described by Jiang et al. (1993b). Simultaneously, $Cu(NH_3)_2^{+}$ is converted to $Cu(S_2O_3)_3^{5-}$ ions and oxidised to $Cu(NH_3)_4^{2+}$ with oxygen (Wan, 1997). The predominant cathodic reaction depends upon the relative concentrations of the species in solution (Eqs. 2.64, 2.65 and 2.69).

$$Cu(NH_3)_2^{+} + 3S_2O_3^{2-} = Cu(S_2O_3)_3^{5-} + 2NH_3 \quad (2.69)$$

In addition, the $Cu(NH_3)_4^{2+}$ ions gain electrons from both $S_2O_3^{2-}$ and Au, as described by Eq. 2.28 (in Table 2.3) and Eq. 2.70, leading to the oxidation of $S_2O_3^{2-}$.

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} = 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \quad (2.28)$$

$$Cu(NH_3)_4^{2+} + Au = Cu(NH_3)_2^{+} + Au(NH_3)_2^{+} \quad (2.70)$$

(vi) Breuer and Jeffrey (2002) noted that, if Eqs. 2.61 and 2.62, proposed by Jiang et al. (1993b), were rate controlling, the reactions would still occur without thiosulfate. This would result in a measurable current in the appropriate potential region even in the absence of thiosulfate, a feature that was not observed in practice. They claimed that ammonia could form a mixed gold-ammonia-thiosulfate complex, such as $Au(S_2O_3)(NH_3)^{-}$ proposed by Wang (1992), or that ammonia affects the surface of the gold electrode in some other way.

(vii) Zhang and Nicol (2003) noted that:

(a) in the absence of thiosulfate, the anodic current for gold oxidation was negligible in an aqueous ammonia solution, and

(b) the addition of ammonia to the thiosulfate solution resulted in an increase in gold dissolution as well as elimination of the passivating (sulfur) film.

In summary, there has been little progress on defining the reaction mechanism for the dissolution of gold in a Cu(II)-NH_3-$S_2O_3^{2-}$-O_2 system, largely due to the lack of knowledge of exact species involved on the gold surface and in solution. Recent work by Senanayake et al. (2003) and Perera and Senanayake (2004) have confirmed the stability order of the gold(I) complexes $Au(S_2O_3)_2^{3-}$ > $Au(S_2O_3)(NH_3)^-$ > $Au(NH_3)_2^+$. Senanayake (2004a) showed the importance of considering the involvement of $Cu(NH_3)_p(S_2O_3)_n^{-2(n-1)}$ (p = 2,3 ; n = 1,2) in the oxidation of both thiosulfate and gold by ammoniacal copper(II) solutions. Wensveen and Nicol (2005) confirmed the formation of an intermediate copper(II)-ammonia-thiosulfate complex which is responsible for the oxidation of thiosulfate by copper(II). Black (2006) confirmed the formation of mixed copper(I)-ammonia-thiosulfate complexes.

2.7 Aims of present study

The aims of the present study are to obtain experimental results with gold colloids and powders, and analyse and report:

(i) the gold(I), copper(I) and copper(II) speciation,

(ii) the effect of concentration of principal reagents and various background salts that are important in the thiosulfate leaching process for gold,

(iii) the effect of pH and temperature of solution,

(iv) the effect of particle size of gold colloids and gold powders,

(v) the shrinking sphere and shrinking core kinetic models in:

(a) copper-free oxygenated ammoniacal thiosulfate solutions,

(b) oxygen-free ammoniacal copper(II)-thiosulfate solutions in the absence or presence of background electrolytes, and

(c) oxygenated ammoniacal copper(II)-thiosulfate solutions.

CHAPTER 3 EXPERIMENTAL

3.1 Materials and reagents

All reagents were of analytical grade. Millipore water was used throughout the experiments. Table 3.1 gives a list of materials and reagents used in the experiments described in this thesis.

Table 3.1 *List of materials and reagents*

Reagents	Formulae	Purity	Purpose
Copper Sulfate	$CuSO_4.5H_2O$	AR	Oxidation of gold
Ammonium Sulfate	$(NH_4)_2SO_4$	AR	pH/ionic strength adjustments
Sodium Thiosulfate	$Na_2S_2O_3$	AR	Gold lixiviant
Sodium Sulfate	Na_2SO_4	AR	Adjust ionic strength
Sodium Hydroxide	NaOH	AR	Adjust pH
Sulfuric Acid	H_2SO_4	AR	Adjust pH
Ammonia	NH_3	AR	Form $Cu(NH_3)_4^{2+}$ ion
Sodium Cyanide	NaCN	AR	Effect on gold dissolution
Sodium Sulfite	Na_2SO_3	AR	Effect on gold dissolution
Sodium Chloride	NaCl	AR	Effect on gold dissolution
Sodium Carbonate	Na_2CO_3	AR	Effect on gold dissolution
Sodium Nitrate	$NaNO_3$	AR	Effect on gold dissolution
Lead (II) Nitrate	$Pb(NO_3)_2$	AR	Effect on gold dissolution
Silver Nitrate	$AgNO_3$	AR	Effect on gold dissolution
Potassium Chloride	KCl	AR	Reference electrode
Nitrogen Gas	N_2	High purity	Depletion of oxygen
Oxygen Gas	O_2	High purity	Oxidation of gold
Sodium Chloroaurate	$NaAuCl_4H_2O$	Lab. chemical	Preparation of gold colloids
Gelatine		Lab. chemical	Preparation of gold colloids
Ascorbic Acid	$C_6H_8O_6$	AR	Preparation of gold colloids
Hydrochloric Acid	HCl	AR	Titration of ammonia
Potassium Iodate	KIO_3	AR	Titration of thiosulfate
Potassium Iodide	KI	AR	Titration of thiosulfate

3.2 Preparation of gold colloid

3.2.1 Unstabilized gold colloid

Unstabilized gold colloid was prepared by the reduction of gold(III) chloride with sodium citrate in aqueous solution (Turkevich et al., 1951). This method can be used for the preparation of monodisperse gold suspensions with widely different particle diameters. The procedure is described below:

(1) A sample of 8.0 mg of $NaAuCl_4.2H_2O$ was dissolved in 75 ml water, and then heated to boiling.

(2) Various volumes of 1.0% sodium citrate reductant between 0.16 ml and 1.00 ml were added to the boiling solution, depending on the required particle diameter. Table 3.2 shows how the particle size varies with increasing amounts of sodium citrate.

(3) The colour of the boiling solution changed after 100 seconds to 150 seconds. The boiling was continued until the colour no longer appeared to change with time (about 5 minutes).

(4) The colloid was diluted to 100 ml to produce a suspension containing 0.2 mM gold colloid.

(5) The pH of the solution was adjusted to 11.0 by adding crushed solid NaOH pellets.

Unstabilized gold colloid can flocculate in high concentrations of background salts or if left in storage for a long time. The wavelength of the absorption peak and absorbance of unstabilized gold colloid also changes with time, see Table

3.3. The gold colloid was stored in a brown bottle in a cool room at a temperature of 3ºC - 5ºC.

Table 3.2 *Effect of amount of sodium citrate on the particle size and colour of gold colloids*

Sodium citrate (1%) (ml)	Particle diameter (nm)	Colour
1.00	16	Orange
0.75	25	Red
0.50	41	Red
0.30	72	Dark red
0.21	98	Violet
0.16	147	Violet

$NaAuCl_4$ concentration is 0.2 mM, boiling, pH 11.0 (Frens, 1973).

3.2.2 Stabilized gold colloid

Stabilized gold colloid in the presence of gelatine was used in most of the experiments. The procedure for preparation was as follows:

(1) A solution containing 100 ml of Millipore water and 0.1 g of gelatine was heated to about 40°C on a hotplate while stirring until the gelatine dissolved.

(2) The solution was cooled to room temperature, and then the pH was adjusted to a value between 7 and 10 (Gelatine hydrolyses at pH values higher than 10).

(3) The solution was then brought to boiling and 20 mg of $NaAuCl_4.2H_2O$ was added, followed by 5.0 ml of freshly prepared 1% w/v ascorbic acid.

(4) The solution was heated for about 30 minutes during which time the colour changed to dark red/purple.

(5) After cooling to room temperature the solution was diluted to 250 ml and the pH was adjusted to 6.5 - 7.0. The concentration of gold colloid was 0.2 mM (about 40 mg/l). The stabilized gold colloid can be stored for a few months in a cool room at 3ºC to 5ºC, see Table 3.3.

3.2.3 Silver colloid

The method used for preparation of silver colloid (Pal and Ganguly, 1987) was as follows:

(1) 5.0 ml of 0.01 M $AgNO_3$ solution was placed in a 250 ml beaker, 50 ml of 1% gelatine solution was added with stirring.

(2) The pH of the solution was adjusted to about 8 using 0.2 M NaOH solution.

(3) The solution was reduced with 5.0 ml of 1% ascorbic acid and diluted to 100 ml.

The concentration of silver colloid was 0.5 mM. The silver colloid suspension is stable in an amber bottle at room temperature.

3.3 Determination of particle size

Transmission Electron Microscopy (TEM) (Philips CM100 Biotwin) was used to determine the particle size distribution of the gold colloids. A sample (2.5 μl) of 3 mM gold colloid was placed on a Formvar coated grid, dried on a filter paper, photographed at a magnification of 105,000 times and the sizes measured at random with a micro comparator. Figs. 3.1a and b show two of the electron micrographs of the colloid particles.

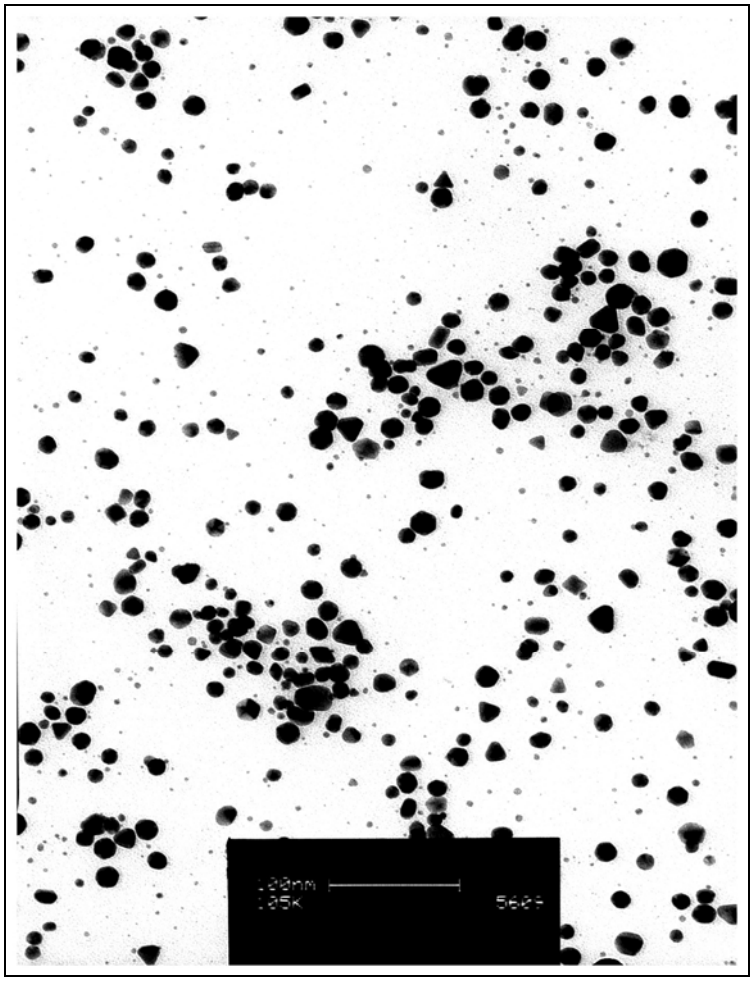


Fig. 3.1a *Transmission electron micrographs of gold colloid particles (x 105,000).*

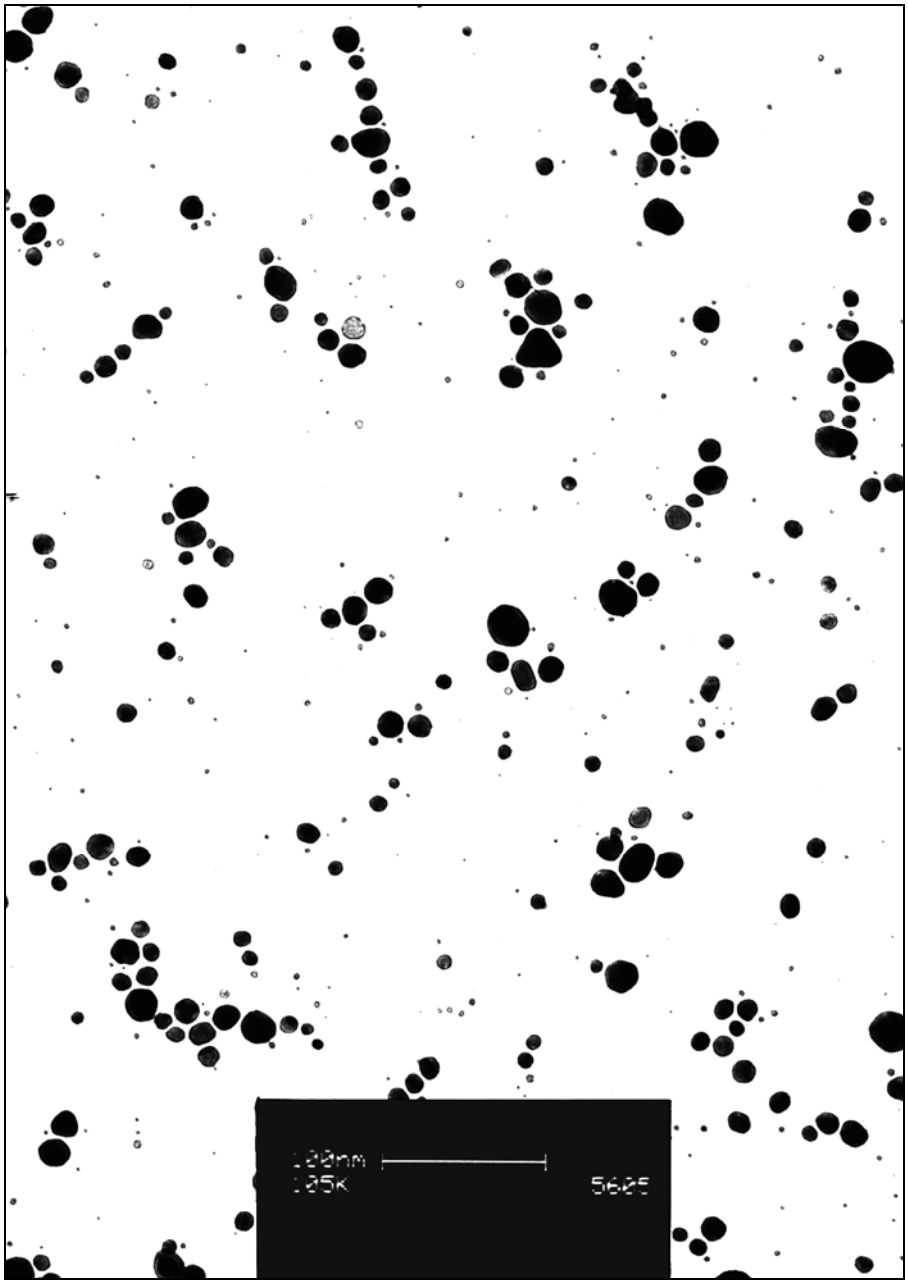


Fig. 3.1b *Transmission electron micrographs of gold colloid particles (x 105,000).*

3.4 Reaction vessels and experimental measurements

3.4.1 Reaction vessels

The oxidation of gold colloids in the presence or absence of copper(II) and the reduction of copper(II) by thiosulfate were carried out in two 100 ml glass vessels with water jackets in which the solutions were magnetically stirred, as shown schematically in Fig. 3.2. The variation of gold colloid concentration with time was monitored in vessel 1 whilst the residual concentration of copper(II) in the absence of gold colloids was monitored in vessel 2.

Experiments with gold powder in the copper(II)-ammonia thiosulfate system were carried out in a 1 litre glass vessel with a water jacket in which the solution was mechanically stirred, as shown in Fig. 3.3.

Fig. 3.2 *Experimental set up for gold colloid oxidation*

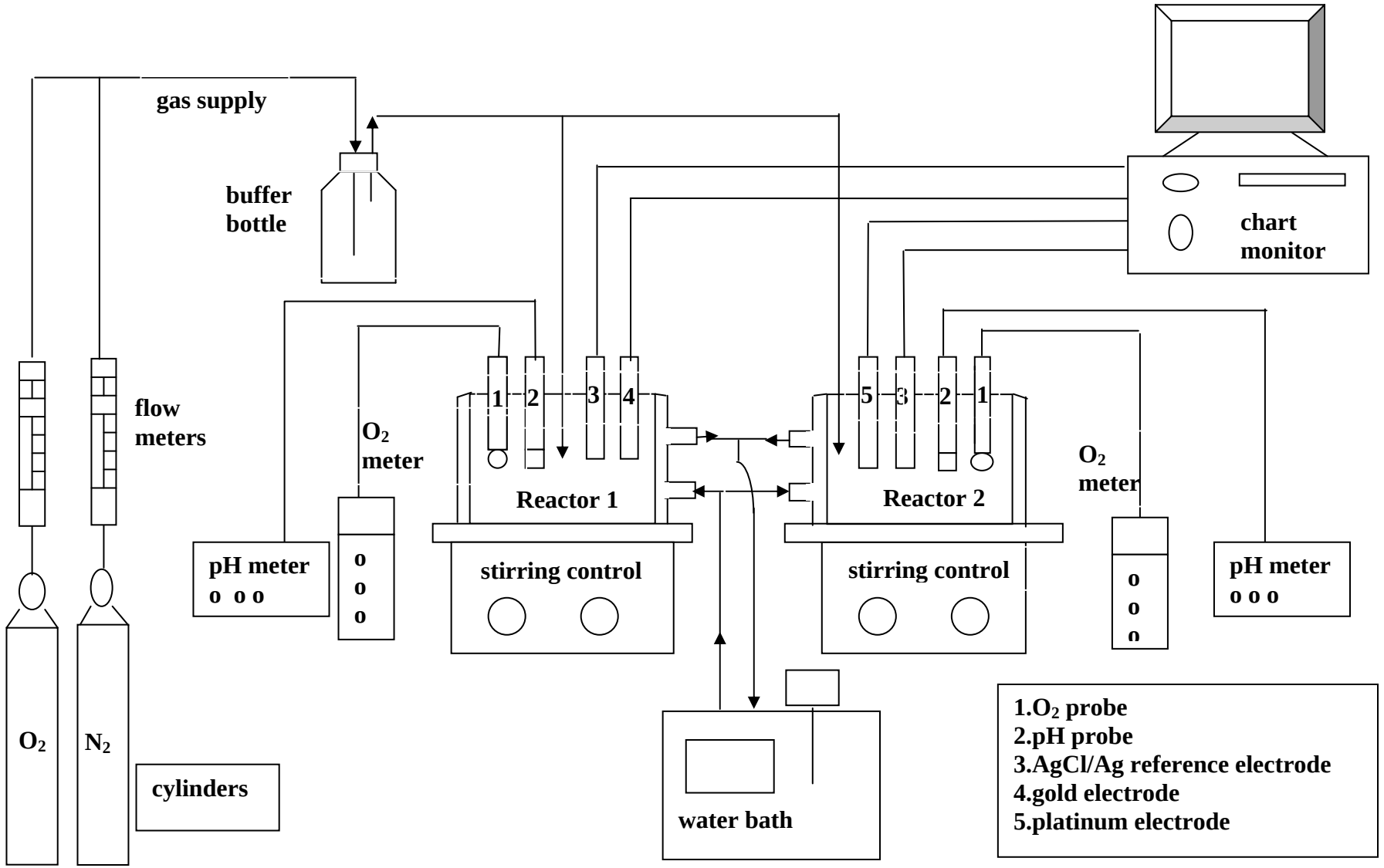
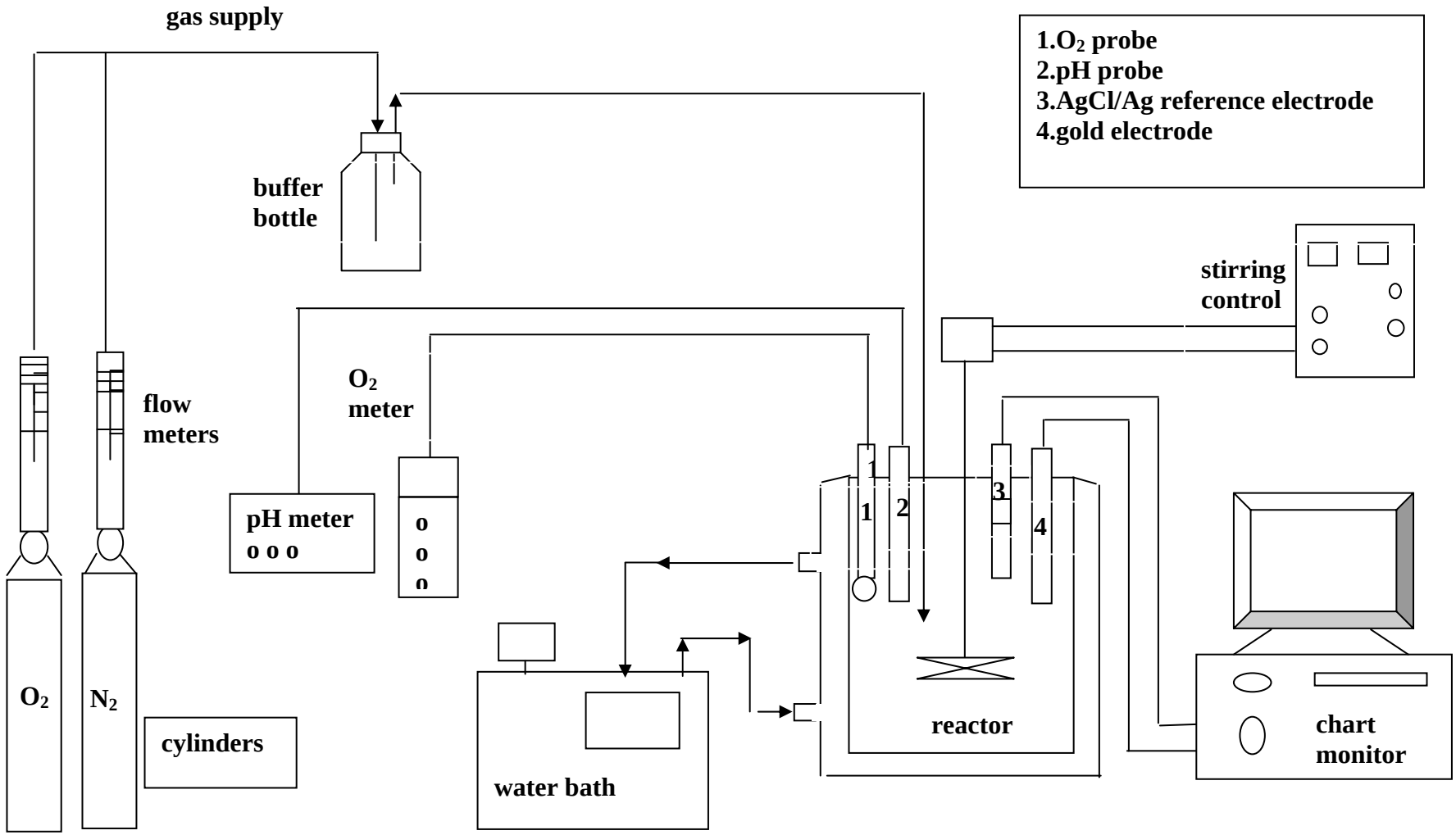


Fig. 3.3 *Experimental set up for gold powder oxidation*



3.4.2 Temperature and pH

The temperature of reaction solution(s) was controlled using a water bath (Ratek thermo regulator Model No. TH5-2 kW), and temperature was maintained to within 0.1ºC of the desired value. A pH probe with a built in Ag/AgCl/Cl^- refillable reference electrode (Orion pH/Eh meter, Model 420A) was used to measure solution pH. The pH value was manually controlled at the desired value by the addition of sulfuric acid or sodium hydroxide. Due to the use of an ammonia-ammonium ion buffer system, the solution pH was generally stable at the desired pH value up to 11.0 during the period of reaction. The ionic strength of the solutions was adjusted at the beginning of the experiment by adding 1.0 M Na_2SO_4.

3.4.3 Oxygen concentration

The dissolved oxygen concentration was measured with a digital oxygen meter (Syland Model 4000) for vessel one and a Jenway 970 DO_2 Meter for vessel two. For experiments performed under nitrogen, the readings on the meters were zero.

3.4.4 Redox potentials

During the experimental runs the potentials were continuously monitored using two Ag/AgCl/Cl^- reference electrodes, a gold electrode (gold oxidation), and a platinum electrode (copper(II) reduction). The electrodes were connected to a

data acquisition system controlled by Labview. A sodium sulfate salt bridge with the same ionic strength as that of the test solutions was used to avoid contamination to the test solution and to maintain a fixed liquid junction potential. The measured cell potentials ($E_{measured}$) were converted to values against the standard hydrogen electrode using the relationship:

$E = E_{measured} + 199$ mV (25ºC) ($E = E_{Au}$ or E_{Pt}) (3.1)

The potential of the AgCl/Ag reference electrode was frequently checked against a standard calomel electrode. For temperatures (T) other than 25ºC, a temperature coefficient of dE/dT = -1.01 mV/K for a saturated KCl, AgCl/Ag electrode was used for potential correction (Reiger, 1994).

E (T, satd.KCl, AgCl/Ag electrode) = 199 - 1.01T (mV) (3.2)

Although the rate of magnetic stirring had no effect on the measured potentials the stirring rate was maintained constant throughout all the experiments.

3.4.5 Nitrogen flow rate

Most experiments were carried out under nitrogen. A set of experiments was carried out to decide the minimum nitrogen flow rate for 100 ml vessels in order to maintain oxygen concentration of zero in solution. Fig. 3.4 shows the decrease in concentration of oxygen in solution with time at different flow rates of nitrogen. It is clear that a flow rate of at least 60 ml/minute to 80 ml/minute is needed to keep the oxygen concentration at zero in each solution. A higher flow

rate of nitrogen is detrimental due to excessive loss of ammonia, therefore a flow rate of 80 ml/minute was chosen. Nitrogen gas was passed through 500 ml of a solution with the same composition as that of the test solution in order to minimize the loss of ammonia.

A flow rate of 150 ml/minute was chosen for the 1 litre vessel to maintain oxygen concentration at zero. All the gas flow rates were measured using a flow meter (Platon 1.BD. range 0 ml/minute to 250 ml/minute).

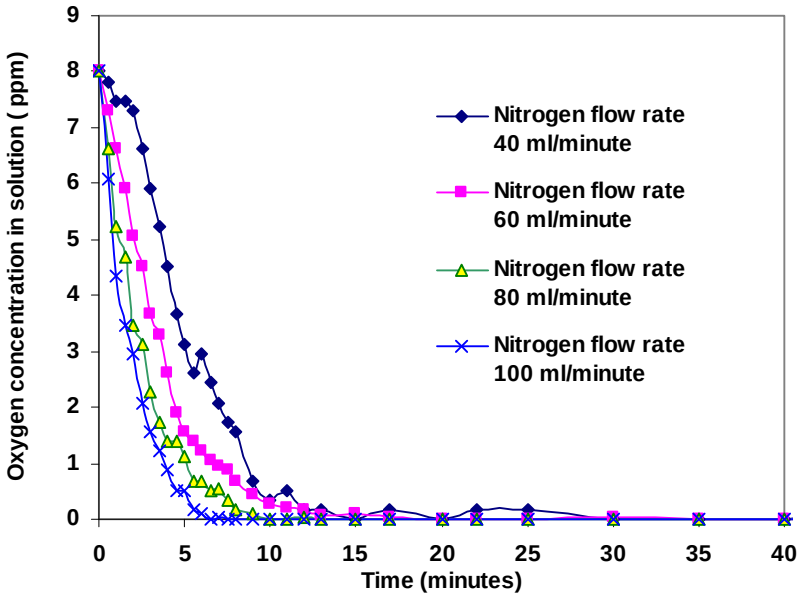


Fig. 3.4 *Effect of nitrogen flowrate on de-oxygenation of reaction solution.*

3.4.6 Thiosulfate concentration

The thiosulfate concentrations in solution were determined using a standard iodometric titration (Bassett et al., 1978).

3.4.7 Sampling

Two 5 ml syringes were used to take solution samples from two reaction vessels for the measurement of absorbance during the period of reaction. For the experiments with gold powder, a 10 ml syringe was used to take solution samples from the 1 L vessel through a membrane filter. The type of filter paper used was mixed cellulose ester A020A025A, 25, with a filter paper pore size of 0.2 μm and a diameter of 25 mm.

3.5 UV-Visible spectra of gold, silver, and copper

3.5.1 Measurement of absorbance

A MultiSpec-1500 (SHIMADZU) UV-visible spectrophotometer connected to a computer was used to measure the absorbance of the test solutions at different time intervals. A cuvette of 20 mm optical path length was used in most experiments; but for the cyanidation reaction, a cuvette of 10 mm optical path length was used. The 0.2 mM (≈ 40 mg/l) gold colloids gave an absorbance maximum of about 1.6 at a wavelength of 530 nm. The value of λ_{max} depends on the stirring speed, temperature, and the amount of ascorbic acid added. The latter affected the particle size (see Table 3.2). The 0.5 mM silver colloids gave an absorbance of about 2.5 (10 mM optical path cuvette) at 415 nm to 420 nm.

3.5.2 Comparison of UV-visible spectrum of Au(c), Au(I), Cu(II) and Cu(I)

In solutions of pH 9 - 10, copper(II) exists predominantly as the $Cu(NH_3)_4^{2+}$ species. The precipitation of copper(II) occurs at pH values of about 11. The copper(II) tetraammine ion and stabilized gold colloids examined in the present study have absorption peaks at λ_{max} = 610 nm and 530 nm respectively. However, the reaction products $Au(S_2O_3)_2^{3-}$ and $Cu(S_2O_3)_3^{5-}$ (Eqs. 1.4 and 1.5) have negligible absorbance in this region as shown in Fig. 3.5 and Fig. 3.6, and can be ignored. Likewise Ag(I)-NH_3-$S_2O_3^{2-}$ solutions show no absorbance in this region (Perera and Senanayake, 2004). Fig. 3.7 shows the changes of the spectrum upon the addition of $Na_2S_2O_3$ to a solution of $Cu(NH_3)_4^{2+}$. The two peaks at 610 nm and 335 nm in Fig. 3.7 are due to $Cu(NH_3)_4^{2+}$ and a mixed complex of Cu(II)-NH_3-$S_2O_3^{2-}$ respectively. Thus, a comparison between Figs. 3.5, 3.6 and 3.7 shows the need for a background correction for the absorbance of copper(II), as a result of the overlap of the peak due to $Cu(NH_3)_4^{2+}$ with that of gold colloid at 530 nm.

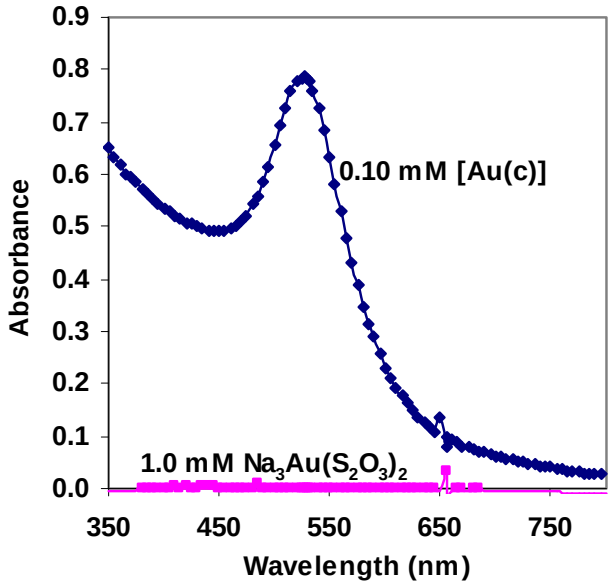


Fig. 3.5 *Comparison between UV-Visible spectra of stabilized gold colloid and gold-thiosulfate complex. [Au(c)] = 0.1 mM, [$Na_3Au(S_2O_3)_2$] = 1.0 mM.*

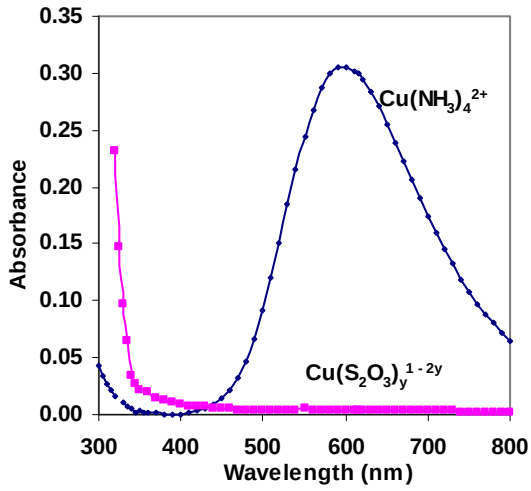


Fig. 3.6 *Comparison between UV-visible spectra of copper(II) tetraammine and copper(I)-thiosulfate complex.*
[Cu(II)] = 1.5 mM, [NH_3 +NH_4^+] = 240 mM; [$Na_2S_2O_3$] = 95 mM.
1 hour after mixing copper(II), ammonia and thiosulfate.

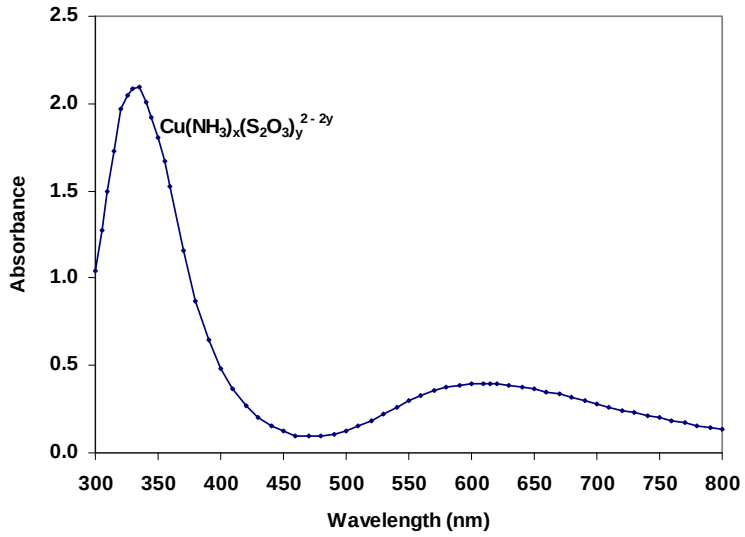


Fig. 3.7 *UV-visible spectrum for the Cu(II)-NH_3-$S_2O_3^{2-}$ system*
[Cu(II)] = 3.0 mM, [NH_3 + NH_4^+] = 240 mM, [$Na_2S_2O_3$] = 50 mM,
40 seconds after mixing copper(II) tetraammine and thiosulfate.

3.5.3 Comparison between unstabilized and stabilized gold colloids

Figures 3.8 and 3.9 show that the peak wavelength varies from 520 nm to 550 nm and from 525 nm to 540 nm respectively with increasing particle size for unstabilized or stabilized gold colloids. Figures 3.10 - 3.11 compare the UV-Visible spectra of the stabilized and unstabilized gold colloids. Table 3.3 lists the absorbance of the suspensions at various times after preparation. The gelatine stabilized suspension exhibited a greater stability and was therefore used in most experiments.

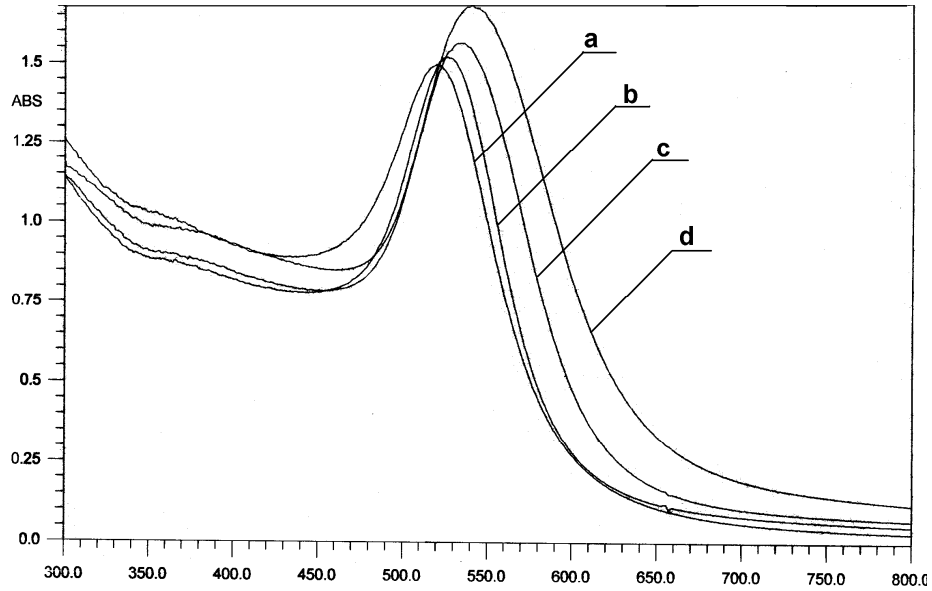


Fig. 3.8 *Effect of particle size on UV-visible spectrum of unstabilized gold colloids.*

[Au(c)] = 0.1 mM, particle size: a) 15 nm, b) 20 nm, c) 30 nm, d) 35nm.

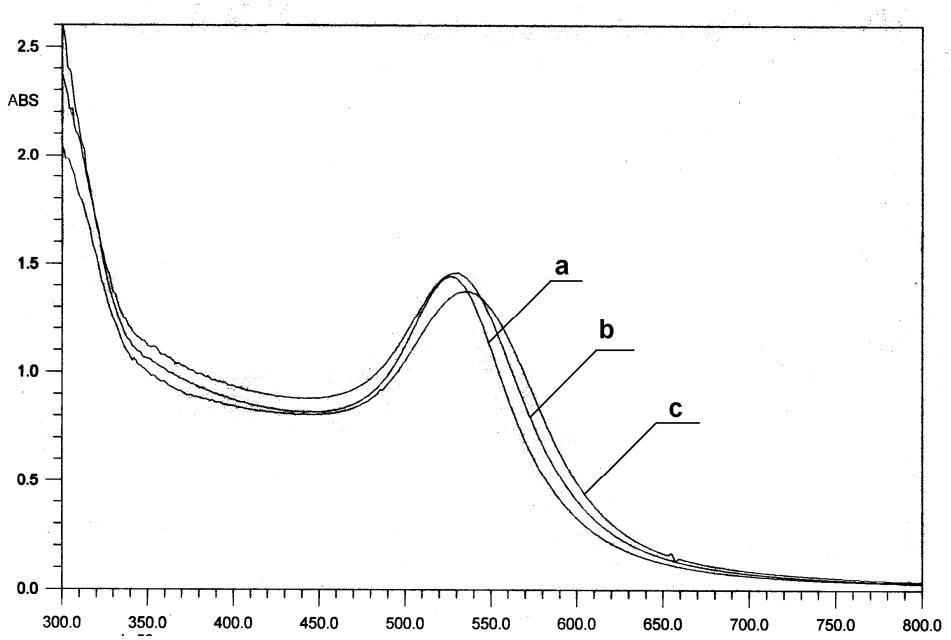


Fig. 3.9 *Effect of particle size on UV-visible spectrum of stabilized gold colloids.*

[Au(c)] = 0.1 mM, particle size: a) 20 nm, b) 25 nm, c) 30 nm.

Table 3.3 *Stability of gold colloid upon storage*

Days	Change in maximum absorbance (%) Gelatine stabilized colloid	Change in maximum absorbance (%) Unstabilized colloid
7	0.2	1.0
43	2.0	9.9
143	3.5	22.0

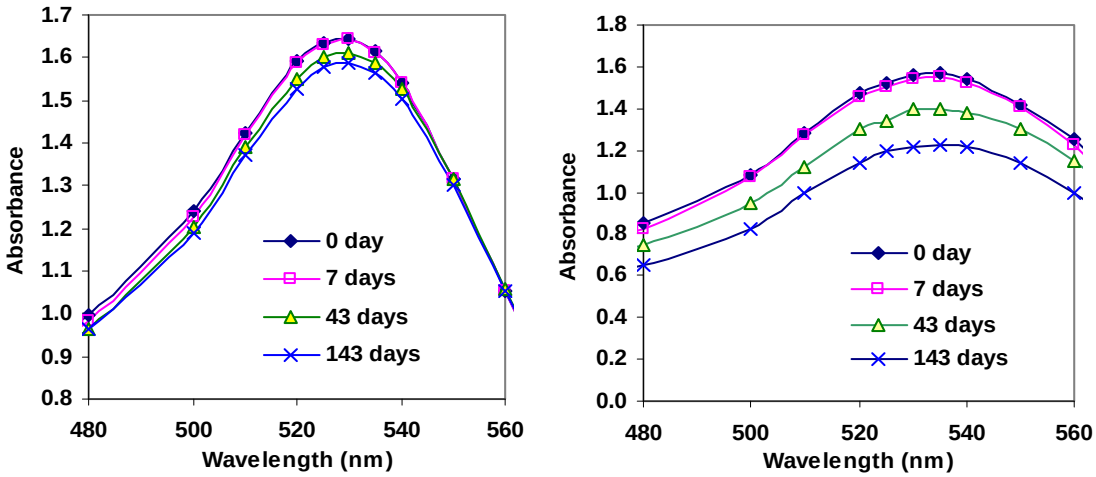


Fig. 3.10 *Effect of storage time on UV-visible spectrum of stabilized gold colloids.*

Fig. 3.11 *Effect of storage time on UV-visible spectrum of unstabilized gold colloids.*

[Au(c)] = 0.2 mM, storage temperature 3 - 5ºC, 20 mm cuvette.

Stabilized gold colloid was used to test the effect of the nature and concentration of background electrolytes and aeration. Fig. 3.12 shows that stirring under nitrogen or air had no influence on the stability of gold colloids in the absence of sodium sulfate. However, the addition of sodium sulfate background electrolyte influenced the spectrum. For example, the change in absorbance value of gold colloids in 5 hours (open to air) was between 0.7% and 6% when the concentration of background Na_2SO_4 was increased from 0

M to 0.67 M (ionic strength 0 to 2.0). Thus, as is well known, a high ionic strength affects the stability of gold colloids. An ionic strength of 0.5 was chosen for most experiments.

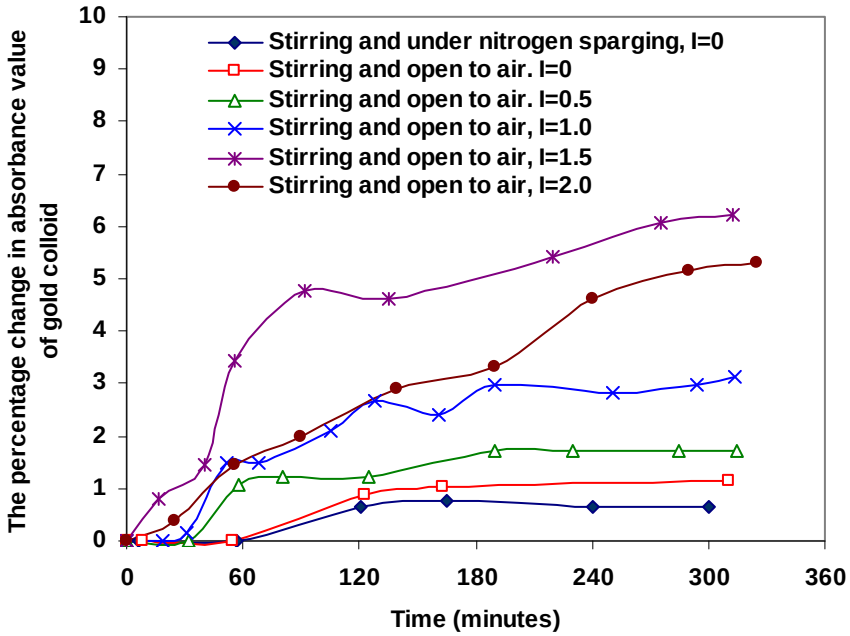


Fig. 3.12 *Effect of ionic strength and air on percentage change in UV-visible absorption of stabilized gold colloids.*

3.5.4 Beer-Lambert Law

Two sets of experiments were performed to confirm that the gold colloids and copper(II) solutions obeyed the Beer-Lambert Law. The absorbances value of gold colloids and copper(II) solutions were found to be directly proportional to concentrations of gold and copper(II) under the experimental conditions ([Au(c)] $\leq$ 0.2 mM, [Cu(II)] < 5 mM). The data in Figs. 3.13 and 3.14 confirm this relationship. Thus, the concentrations of gold colloid and copper(II) can be determined from their initial concentrations $[Au(c)]_o$, $[Cu(II)]_o$ and their absorbance value {A} at time t as shown in Eqs. 3.3 and 3.4.

$$[Au(c)]_t = [Au(c)]_0 * (\{A\}_{Au(t)} / \{A\}_{Au(0)}) \quad (3.3)$$

$$[Cu(II)]_t = [Cu(II)]_0 * (\{A\}_{Cu(t)} / \{A\}_{Cu(0)}) \quad (3.4)$$

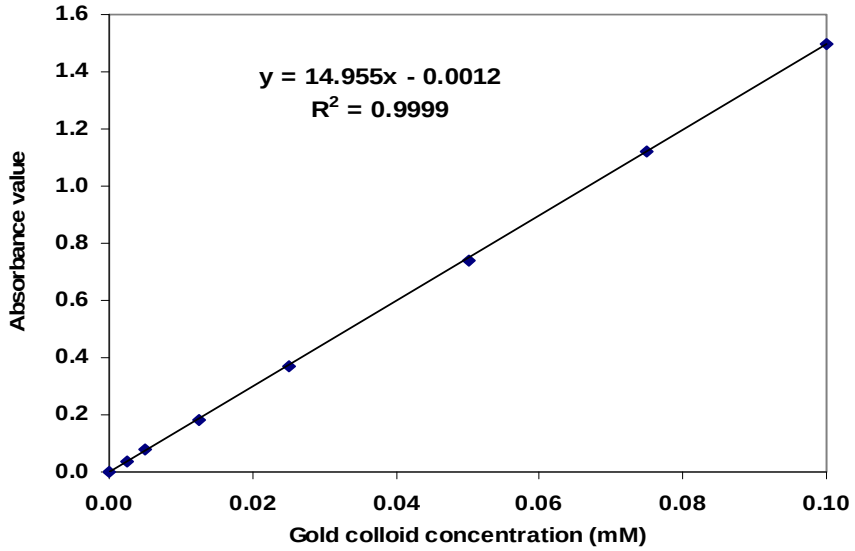


Fig. 3.13 *Verification of the Beer-Lambert Law for gold colloids. (Measured after diluting a stock solution of [Au(c)] = 0.1 mM).*

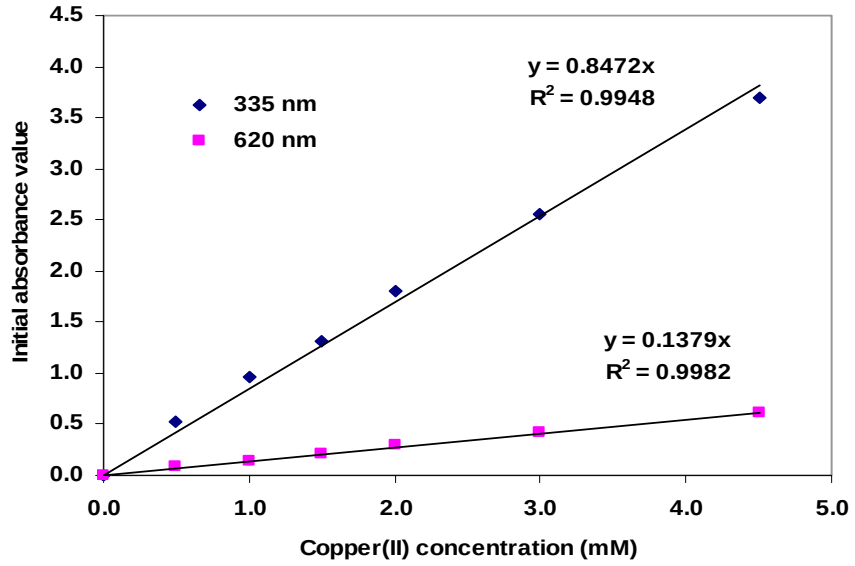


Fig. 3.14 *Verification of the Beer-Lambert Law for copper (II). [NH_3+NH_4^+] = 240 mM, [$Na_2S_2O_3$] = 50 mM.*

3.5.5Correction for background absorbance due to copper(II)

As shown in Fig. 3.15, the measured UV-Visible spectra of gold colloids and silver colloids in thiosulfate free solutions are affected by the presence of $Cu(NH_3)_4^{2+}$ and other copper species that have a measurable absorbance in the same wavelength range. The decrease in absorbance at 530 nm with time shown in Fig. 3.16 is a result of the decrease in concentration of both the gold colloids and copper(II) (Eq. 3.5);

$$A\{\text{reaction mixture}\}_{530\ nm} = A\{Au(c)_{530\ nm}\} + A\{Cu(NH_3)_4^{2+}{}_{530\ nm}\} \quad (3.5)$$

Where A = absorbance.

Therefore, there are two issues to be addressed in relation to the analysis of solutions used in kinetic experiments in order to determine the absorbance of gold colloid at various times:

(i) extrapolation of data to t = 0 to obtain the initial absorbance,$\{A\}_{530\ nm,\ t = 0}$ (Eqs. 3.3 and 3.4)

(ii) correction for background absorbance due to copper(II) at a given time (Eq. 3.5).

In kinetic experiments, t = 0 was taken as the time at which sodium thiosulfate was added to the reaction mixture solutions. Fig. 3.16 shows a linear relationship between the absorbance measured during the first few minutes and time. Extrapolation of these plots to t = 0 gives the values of $A\{\text{reaction mixture}\}_{t=o}$.

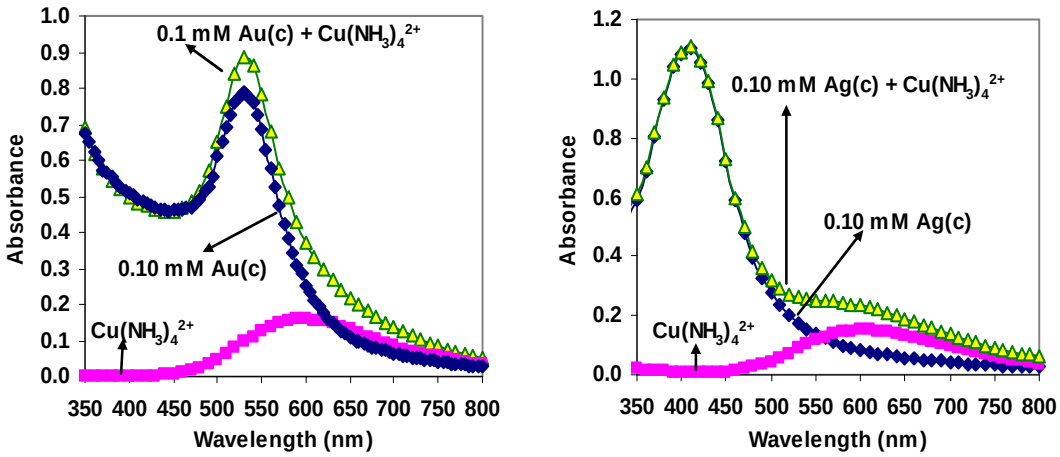


Fig. 3.15 *UV-visible spectra for gold colloids, silver colloids, $Cu(NH_3)_4^{2+}$ and a mixture of colloids and $Cu(NH_3)_4^{2+}$.*
(0.1 mM Au(c), 0.1 mM Ag(c), 1.5 mM Cu(II), 240 mM total ammonia, pH 9.3).

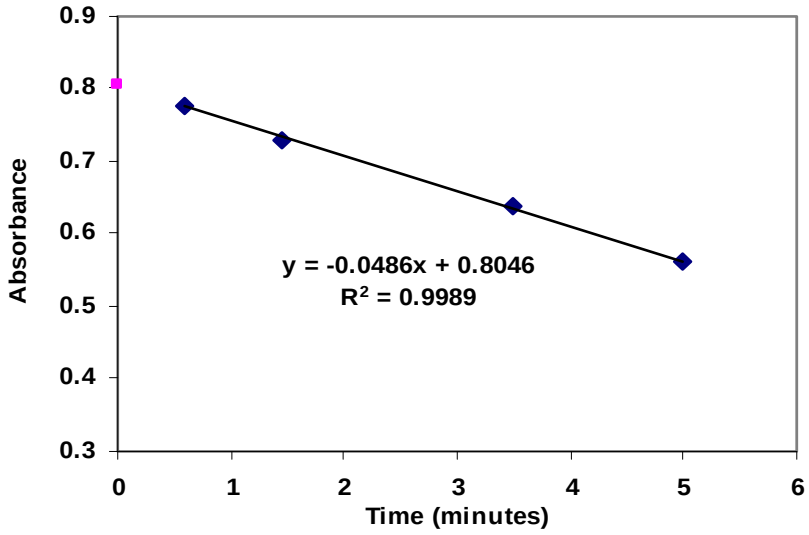


Fig. 3.16 *Variation of absorbance with time in a typical reaction solution.*
(0.1 mM Au(c), 1.5 mM Cu(II), 240 mM total ammonia, pH 9.3).

The absorbance due to copper (II) tetraammine complex ions was determined using a blank experiment conducted in a gold free solution. Since the concentration of gold colloids was much less than that of copper(II), it was assumed that gold colloids did not affect the kinetics of the reaction of copper(II) tetraammine with thiosulfate. The rate of this reaction can thus be assumed to be the same in both vessels. Therefore, the contribution of copper(II) to the absorbance at 530 nm from a blank experiment conducted at the same time in a parallel reactor was used in Eq. 3.6 to calculate the absorbance due to gold colloids at any time t:

$$A_t\{Au(c)\}_{530nm} = A_t\{\text{Reaction mixture}\}_{530nm} - A_t\{\text{Blank experiment}\}_{530nm} \quad (3.6)$$

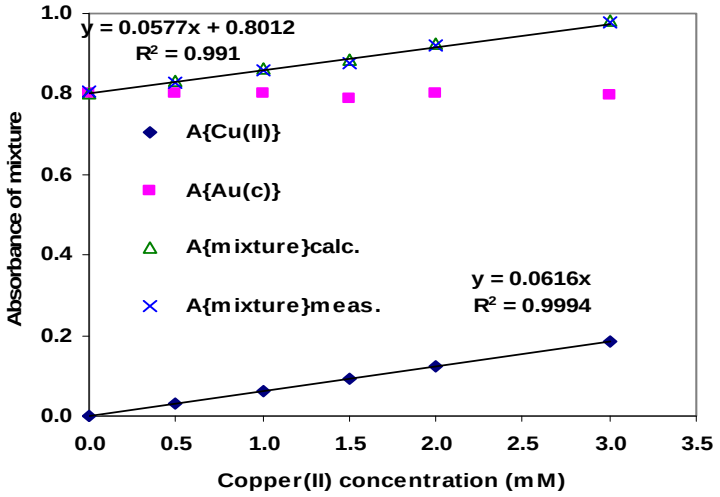
where A_t is the absorbance at time t.

In order to confirm Eq 3.6, experiments were conducted using three sets of solutions: (i) gold colloid, (ii) copper(II) tetraammine sulfate, and (iii) a mixture of (i) and (ii). The measured absorbances in these three cases are listed in Appendix A .1. The sum of the measured absorbance of solutions (i) and (ii) were in good agreement with the calculated value as shown in Fig. 3.17a (low copper) and Fig 3.17b (high copper), with an error of less than about 1%. Further comparisons of absorbance over the wavelength range 480 nm to 650 nm showed the validity of Eq. 3.7.

$$A_t\{Au(c)\}_{480\text{-}650nm} = A_t\{\text{Reaction mixture}\}_{480\text{-}650nm} - A_t\{\text{Blank experiment}\}_{480\text{-}650nm} \quad (3.7)$$

This allows the use of Eqs. 3.6 or 3.7 to calculate the absorbance of gold colloids in the presence of copper(II) tetraammine complex ion. The same method was applied for correction for the background absorbance due to copper(II) in the dissolution of silver colloids in ammonia-thiosulfate solutions.

(a)



(b)

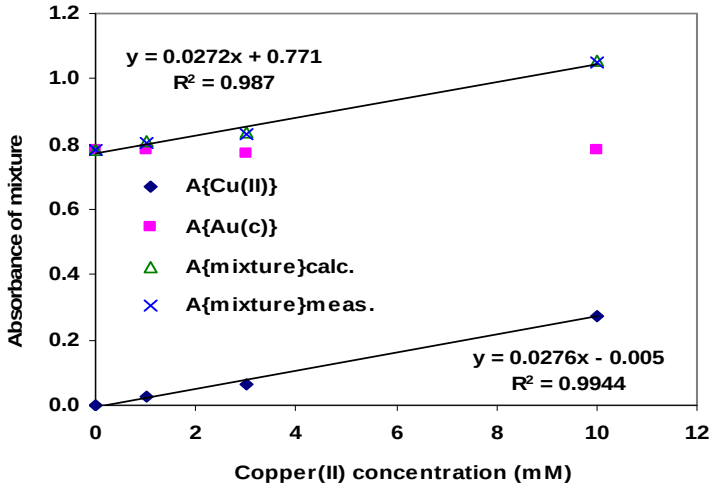


Fig. 3.17 *Effect of copper(II) concentration on initial absorbance of gold colloids at 530 nm (Data from Appendix 1).*

3.6 Experimental procedure for rate studies

3.6.1 Gold colloid-oxygen-cyanide system

Initial kinetic experiments were performed with the gold colloid-cyanide-oxygen system to verify the experimental set-up and procedure through comparisons with published results (McCarthy et al., 1998; Hindmarsh and Nicol, 2001), and to examine the effect of different cyanide concentrations on the rate. The following procedure was adapted:

(i) Adjustment of pH to 10.0 or 11.0 for both cyanide and gold colloid solutions.

(ii) Transfer of 2.4 ml of colloid solution and 0.8 ml of cyanide solution to a cuvette of 10 mm optical path, and recording the UV-visible spectra of the reaction solution with time.

3.6.2 Gold colloid-oxygen-thiosulfate-ammonia system

The general procedure used to perform typical kinetic experiments for gold oxidation in the oxygen-thiosulfate-ammonia system was as follows:

(1) A mixture of solutions containing ammonium sulfate, ammonia, sodium sulfate (and /or other salts), and 25 ml of 0.2 mM gold colloid were transferred to a vessel. The volume in the range 48.0 ml to 49.5 ml was chosen depending on the volume of thiosulfate added later (Step (4)). The absorbance of the solution was recorded.

(2) The vessel was either opened to air or oxygen was bubbled until the dissolved oxygen reached a desired value. In all cases, the oxygen meter reading was taken when the oxygen concentration had stabilized.

(3) The absorbance of the solution and the stable potentials of gold and platinum electrodes were measured at the desired pH (adjusted using H_2SO_4 or NaOH).

(4) The reaction was initiated by the addition of a desired volume of thiosulfate solution to the vessel (t = 0). Sampling and absorbance measurements were carried out every 1 minute to 3 minutes for the first 20 minutes. The electrode potentials, pH, and oxygen reading were also noted. Subsequent sampling and measurements were carried out at time intervals of 5 minutes to 10 minutes, or intervals of 20 minutes to 40 minutes after 1 hour.

(5) In the case of experiments without thiosulfate, gold colloid was added in Step (4) instead of thiosulfate solution.

3.6.3 Gold colloid-copper(II)-thiosulfate-ammonia system

The procedure for experiments carried out for this system was as follows:

(1) a solution of copper(II) sulfate was included in the mixture described in Step (1), in Section 3.6.2.

(2) nitrogen bubbling was continued for about 15 minutes until the oxygen meter reading showed that the concentration of dissolved oxygen was zero.

Steps (3), (4), (5) were the same as in Section 3.6.2.

The procedure for the blank experiments to correct for the reaction of copper (II) tetraammine with thiosulfate in the second vessel was the same as above with the exception that there was no addition of gold colloid. The thiosulfate addition was carried out in Step (4).

3.6.4 Gold colloid-oxygen-copper(II)-thiosulfate-ammonia system

In the case of gold oxidation in oxygenated copper(II)-ammonia-thiosulfate system, the procedure was the same as in Section 3.6.3. Either oxygen or air was used in the place of nitrogen, or the vessel was opened to air.

3.6.5 Gold powder-copper(II)-thiosulfate-ammonia system

The general procedure used to perform a typical kinetic experiment for the oxidation of gold powder in copper(II)-thiosulfate-ammonia solution under nitrogen was as follows:

(1) A solution containing copper sulfate, ammonium sulfate, ammonia, sodium sulfate (and / or other salts) was placed in the reactor and 15.8 mg gold powder of a given particle size range was added. The solution volume was 792 ml.

Steps (2) and (3) were the same as Steps (2) and (3) in Section 3.6.3.

(4) The reaction was initiated by the addition of 8.0 ml of 2.0 M thiosulfate to the reactor (t = 0), so that the total gold represent 20 mg/L. Other details were the same as previously noted. However, the determination of gold

concentrations in solution was carried out using an atomic absorption spectrophotometer (model GBC 933AA).

3.7 Summary of experimental conditions

Tables 3.4 - 3.8 list the experimental conditions used in all the experiments conducted in the present study.

Table 3.4 *Experimental conditions used in Au(c)-oxygen-cyanide systems*

Varied	[Au(c)] mM	$[O_2]$ mM	$[CN]^-$ mM	pH	Oxidant	Ligand
$[CN]^-$	0.075	0.25	0.72-368	10.1-11.1	O_2	CN^-
[Au(c)]	0.0375-0.075	0.25	11.5	11.1	O_2	CN^-
[Au(c)]	0.0375-0.075	0.25	23	11.1	O_2	CN^-
[Au(c)]	0.0375-0.075	0.25	46	11.1	O_2	CN^-

Room temperature.

Table 3.5 *Experimental conditions used in Au(c)-oxygen-thiosulfate-ammonia systems*

Varied	$[O_2]$ mM	$[NH_3+NH_4^+]$ mM	$Na_2S_2O_3$ mM	$[Cl]^-$ mM	pH	Ionic strength	Temp. °C
$[O_2]$	0.06-0.75	240	50	0	9.3	0.5	25
$[NH_3+NH_4^+]$	0.25	67-500	20	0	9.5	0.5	25
$[NH_3+NH_4^+]$	0.25	67-280	0	0	9.5	0.2	25
$[Na_2S_2O_3]$	0.25	200	10-70	0	9.5	0.5	25
$[Na_2S_2O_3]$	0.25	0	10-70	0	9.3	0.21	25
[NaCl]	0.25	120	20	50-330	9.5	0.5	25
[NaCl]	0.25	120	0	50-330	9.5	0.5	25
[NaCl]	0.25	0	20	50-330	9.5	0.5	25
Temperature	0.25	120	20	0	9.5	0.5	25-48

Oxygen as oxidant. [Au(c)] = 0.1 mM; Ligands are ammonia, thiosulfate, chloride, or a combination of them.

Table 3.6 *Experimental conditions used in Au(c)-copper(II)-thiosulfate-ammonia-nitrogen systems*

Varied	[Au(c)] mM	[Cu(II)] mM	[NH_3+NH_4^+] mM	$Na_2S_2O_3$ mM	pH	Ionic strength	Temp. °C
[Au(c)]	0.03-1.5	2	240	50	9.5	0.5	25
[Cu(II)]	0.1	0.5-4.5	240	50	9.3	0.5	25
[Cu(II)]	0.1	0.5-2.5	120	0	9.5	0.5	25
[NH_3+NH_4^+]	0.1	1.5	50-580	20	9.3	0.5	25
[NH_3+NH_4^+]	0.1	1.5	60-240	0	9.5	0.5	25
[$Na_2S_2O_3$]	0.1	1.5	240	10-95	9.3	0.5	25
pH	0.1	2	240	40	8.9-11	0.5	25
Ionic strength	0.1	1.5	60	10	9.5	0.2-1.0	25
Temperature	0.1	2	240	50	9.5	0.5	22-48
Particle size 12-32 nm	0.1	1.5	120	20	9.5	0.5	25
[$AgNO_3$] 0.01-0.15 mM	0.1	1.5	120	20	9.5	0.5	25
[$Pb(NO_3)_2$] 0-0.01 mM	0.1	1.5	120	20	9.5	0.5	25
[$NaNO_3$] 20-330 mM	0.1	1.5	120	20	9.5	0.5	25
[NaCl] 50-330nm	0.1	1.5	120	20	9.5	0.5	25
[NaCl] 50-330nm	0.1	1.5	120	0	9.5	0.5	25
[$Na_2S_3O_6$] 0 or 20 mM	0.1	1.5	120	20	9.5	0.5	25
[$Na_2S_4O_6$] 0 or 5 mM	0.1	1.5	120	20	9.5	0.5	25
[Na_2CO_3] 0 or 110 mM	0.1	1.5	120	20	9.5	0.5	25
[Na_2SO_3] 0 or 40 mM	0.1	1.5	120	20	9.5	0.5	25
[Ag(c)] 0 or 0.1 mM	0.1	1.5	120	20	9.5	0.5	25

Copper(II) as oxidant, under nitrogen.

[Au(c)] = 0.1 mM, ionic strength 0.5(Na_2SO_4).

Ligands are ammonia, thiosulfate, chloride, or a combination of them.

Table 3.7 *Experimental conditions used in Au(c)-copper(II)-oxygen-thiosulfate-ammonia systems*

Varied	[Cu(II)] mM	[NH_3+NH_4^+] mM	[$Na_2S_2O_3$] mM	pH	[O_2] mM
[$CuSO_4$]	1.0-3.0	240	50	9.3	0.31
[$Na_2S_2O_3$]	2.0	240	20-50	9.3	0.31
[O_2]	1.5	240	50	9.5	0.06-0.63

Copper(II) and oxygen as oxidant,

[Au(c)] = 0.1 mM, ionic strength 0.5 (Na_2SO_4).

Ligands are ammonia, thiosulfate, or a combination of them.

Table 3.8 *Experimental conditions used in gold powder-copper(II)-thiosulfate-ammonia systems*

Varied	[Au(s)] mM	[Cu(II)] mM	[NH_3 + NH_4^+] mM	[$Na_2S_2O_3$] mM	pH	Ionic strength	Temp °C
[$CuSO_4$]	0.1	1.5-3.0	120	20	9.5	0.3	25
[NaCl] 0-100 mM	0.1	1.5	120	20	9.5	0.5	25
[$AgNO_3$] 0-0.05 mM	0.1	1.5	120	20	9.5	0.3	25
Powder size 2.25 and 7.25 µm	0.1	1.5	120	20	9.5	0.3	25

Copper(II) as oxidant, under nitrogen.

[Au(s)] = 0.1 mM, ionic strength 0.5 (Na_2SO_4).

Ligands are ammonia, thiosulfate, chloride, or a combination of them.

CHAPTER 4 RESULTS

4.1 Introduction

This Chapter presents the results obtained in experiments conducted with gold colloids or gold powder. Results are presented in the following forms:

(i) curves of percentage of gold dissolution as a function of time,

(ii) curves of measured residual copper(II) concentration as a function of time,

(iii) curves of measured gold (E_{Au}) or platinum (E_{Pt}) electrode potentials corrected to standard hydrogen electrode as a function of time.

Selected results are also presented as tables to highlight variations in gold dissolution, E_{Au} or E_{Pt} due to changes in various parameters such as reagent concentrations, pH, temperature and particle size. Some of the graphical comparisons are made in Appendix 4, and the analyses of all data are presented in Chapters 5 - 7.

4.2 Dissolution of gold colloids in cyanide solutions

In general, the rate of cyanidation of gold according to Eq. 4.1 is dependent upon both cyanide and oxygen concentrations, as well as their relative values. However, the rate of cyanidation of colloidal gold is independent of oxygen concentration in air saturated solutions (McCarthy et al., 1998; Hindmarsh & Nicol, 2001).

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \qquad (4.1)$$

Thus, the oxygen concentration for all experiments described in this section was maintained approximately the same i.e. [O_2] = 0.25 mM (reaction vessels open to air). Figs. 4.1 and 4.2 show the effect of increase in cyanide concentration (0.72 mM - 368 mM CN^-) on the rate of dissolution of gold. The fraction of gold dissolved at a given time increases with increase in the concentration of cyanide up to the highest value studied. Comparison between Fig. 4.1 and Fig 4.2 shows that a decrease in pH from 11.1 to 10.1 and an increase in cyanide concentration increases the rate of gold dissolution. The effect of pH is consistent with the reported rates based on electrochemical method (Dorin and Woods, 1991)

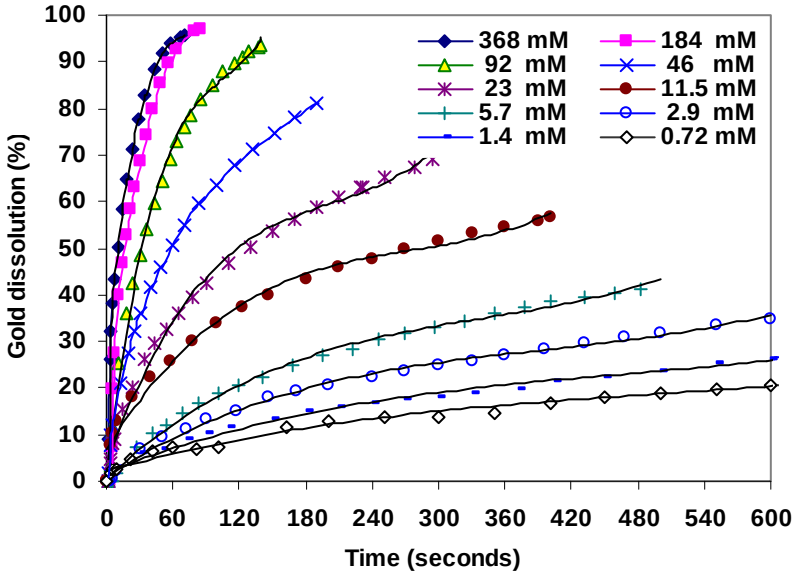


Fig. 4.1 *Effect of cyanide on gold dissolution at variable ionic strengths. Conditions: I < 0.2 (natural), pH = 11.1, [Au(c)]$_i$ = 0.075 mM, [O_2] = 0.25 mM (open to air), 25^{o}C.*

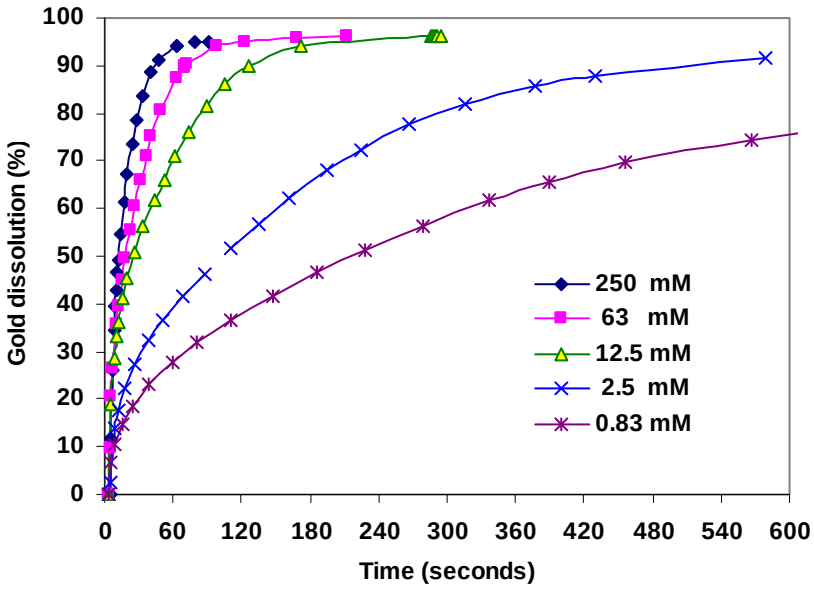


Fig. 4.2 *Effect of cyanide on gold dissolution at ionic strength 0.5. Conditions: I = 0.5 ($NaNO_3$), pH = 10.1, [Au(c)] = 0.075 mM, [O_2] = 0.25 mM (open to air), 25^{o}C.*

4.3 Dissolution of gold in thiosulfate solutions

4.3.1 Effect of oxygen concentration

As shown in Fig. 4.3, the dissolution of gold in thiosulfate solutions free of copper(II) and ammonia is much slower than dissolution in cyanide (Fig. 4.1). In the absence of ammonia, the oxygen concentration did not have a significant effect on the dissolution curve. Moreover, nearly 10% of the reaction occurred in the first 30 minutes followed by a very slow reaction leading to only 14% dissolution after 7 hours (Fig. 4.3). The measured values of the potential of a gold electrode as shown in Fig. 4.4 attained a relatively stable value after about an hour, depending on the oxygen concentration.

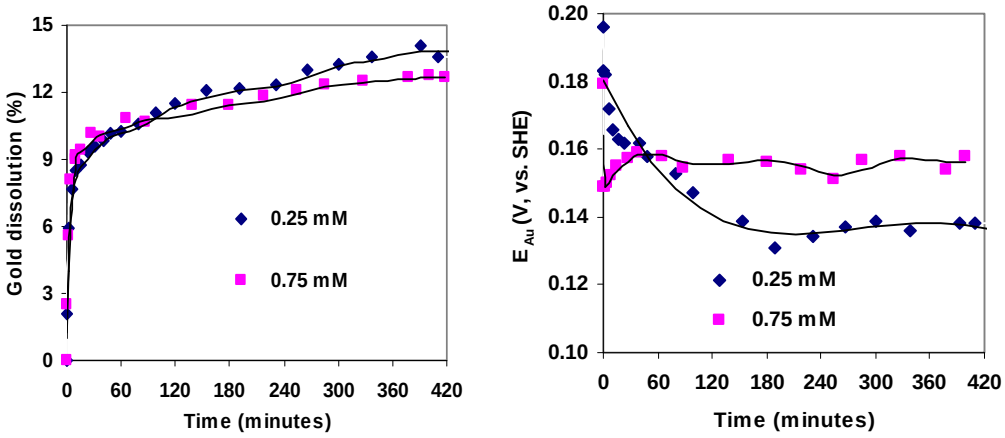


Fig. 4.3 *Effect of oxygen on gold dissolution in non-ammoniacal thiosulfate solutions.*

Fig. 4.4 *Effect of oxygen on gold potential in non-ammoniacal thiosulfate solutions.*

Conditions: [Cu(II)] = 0mM, [NH_3+ NH_4^+] = 0 mM, [$Na_2S_2O_3$] = 50 mM, pH = 9.5, I = 0.15 (natural)

As shown in Fig. 4.5, the extent of gold dissolution was much higher in the presence of ammonia, up to 40% dissolution after 6 hours. This indicates the involvement of ammonia in the surface reaction. An increase in the oxygen concentration also caused an increase in gold dissolution.

Figure 4.6 shows the variation in gold electrode potential during these experiments. In general, a higher oxygen concentration leads to a higher electrode potential and increased gold dissolution. After about 3 hours, the potential becomes relatively stable. A common feature in both Figs. 4.4 and 4.6 is the initial decrease in gold potential soon after the addition of thiosulfate. This is followed by an increase in potential, possibly due to the increase in Au(I) concentration in solution.

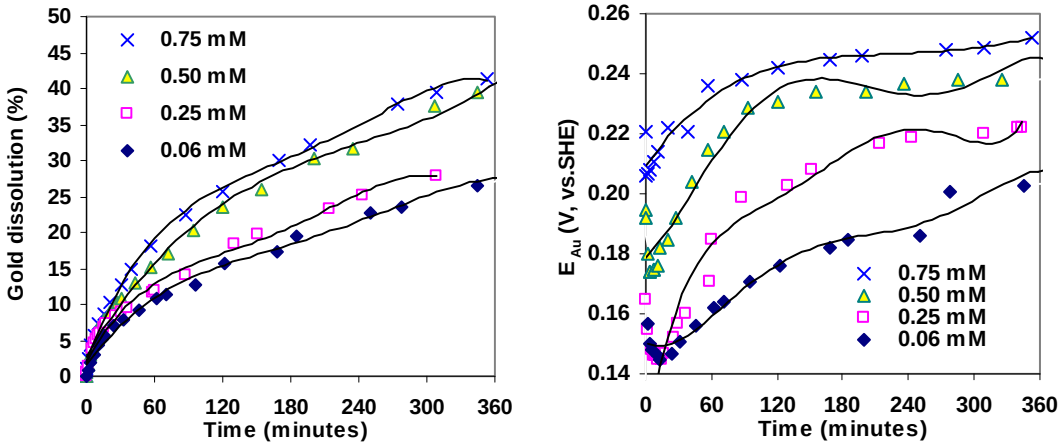


Fig. 4.5 *Effect of oxygen on gold dissolution in ammoniacal thiosulfate solutions.*

Fig. 4.6 *Effect of oxygen on gold potential in ammoniacal thiosulfate solutions. Conditions: [Cu(II)] = 0 mM, [NH_3+NH_4^+] = 240 mM, [$Na_2S_2O_3$] = 50 mM, pH = 9.3.*

4.3.2 Effect of thiosulfate concentration

Table 4.1 compares the two systems: Au(c)-O_2-$S_2O_3^{2-}$ and Au(c)-O_2-NH_3-$S_2O_3^{2-}$, based on the results presented in Appendix A 4.1. It shows that increasing concentration of thiosulfate has no effect on gold dissolution in the absence or presence of ammonia. It is surprising to note that the gold dissolution during the initial 10 minutes is about 9% in the absence of ammonia, but only 4.5% in the presence of ammonia (Table 4.1). However, thereafter, the extent of reaction is much lower than that in the presence of ammonia. Gold potentials are also lower in the absence of ammonia (Table 4.1).

Table 4.1 *Effect of thiosulfate on the dissolution and potentials of gold*

$[Na_2S_2O_3]$ mM	$[NH_3+NH_4^+]$ mM	Ionic strength	Gold dissolution (%) 10 min.	360 min.	E_{Au} (V) 360 min.
10	0	0.21	9	12	0.17
70	0	0.21	9	14	0.13
10	240	0.50	4.5	22	0.22
70	240	0.50	4.5	28	0.22

$[O_2]$ = 0.25 mM, pH = 9.5.

4.3.3 Effect of ammonia concentration

The results of experiments carried out with different ammonia concentrations in the absence or presence of thiosulfate are summarised in Appendix A 4.2. Table 4.2 compares the results after 10 minutes and 6 hours. The effect of the concentration of ammonia on the dissolution of gold is insignificant (2.5% to 4.5%) in the first 10 minutes in both cases. The extent of gold dissolution appears to be less affected by the ammonia concentration in the absence of thiosulfate. However, in the presence of thiosulfate, an increase in ammonia concentration has a positive effect on gold dissolution. The increase in ammonia concentration also caused a small positive effect on gold electrode potentials after six hours (Table 4.2).

Table 4.2 *Effect of ammonia on the dissolution and potentials of gold*

$[Na_2S_2O_3]$ (mM)	$[NH_3+NH_4^+]$ (mM)	Ionic strength	Gold dissolution (%) 10 min.	360 min.	E_{Au} (V) 360 min.
0	67	0.21	2.5	11	0.22
0	280	0.21	4.0	13	0.24
50	67	0.50	3.5	16	0.21
50	500	0.50	4.5	28	0.25

$[O_2]$ = 0.25 mM, pH = 9.5.

In the absence of thiosulfate, there does not appear to be a consistent trend of potential with increasing concentration of ammonia. In the presence of thiosulfate, the potential increased with increasing concentration of ammonia up to 300 mM (Appendix A 4.2).

4.3.4 Effect of chloride concentration

Appendices A 4.3 - 4.5 compare the effect of sodium chloride in the systems: (i) Au-O_2-$S_2O_3^{2-}$ (A 4.3), (ii) Au-O_2-NH_3 (A 4.4), and (iii) Au-O_2-NH_3-$S_2O_3^{2-}$ (A 4.5). In all cases, there was little improvement in gold dissolution as a result of addition of NaCl. The extent of gold dissolution after 7 hours remained lower than 26%, as shown in Table 4.3. The electrode potentials in the absence of ammonia were in the range 0.14 V to 0.17 V, which increased to 0.22 V to 0.25 V in the presence of ammonia. These results are consistent with the results obtained in the absence of chloride (Tables 4.1, 4.2).

Table 4.3 *Effect of chloride on the dissolution and potentials of gold*

[NaCl] (M)	[$Na_2S_2O_3$] (mM)	[NH_3+NH_4^+] (mM)	Gold dissolution (%)			E_{Au} (V)
			10 min.	210 min.	360 min.	360 min.
0	30	0	3.5	7		0.14
0.33	30	0	7.0	11		0.17
0	0	120	1.5		11	0.22
0.33	0	120	4.0		15	0.25
0	30	120	4.5		23	0.24
0.33	30	120	7		26	0.26

[O_2] = 0.25 mM, pH = 9.5.

4.3.5 Effect of temperature

Table 4.4 and Appendix A 4.6 show the effect of temperature on the dissolution and electrode potential of gold. The dissolution after 5 hours is enhanced at higher temperatures, increasing from 23% to 38% as the temperature was increased from 25°C to 48°C. The gold electrode potentials are lower at higher temperatures.

Table 4.4 *Effect of temperature on the dissolution and potentials of gold*

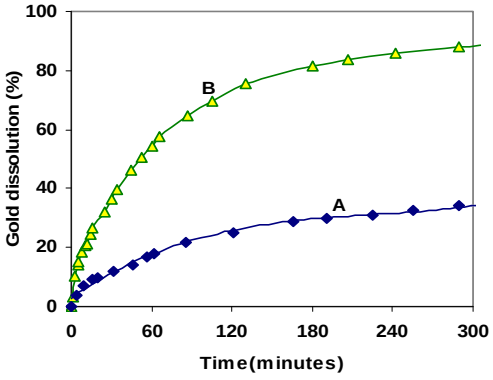
Temperature (°C)	Gold dissolution (%)		Equilibrium potential (V)
	10 min.	300 min.	
25	4.4	23	0.24
30	5.5	27	0.225
40	6.0	32	0.20
48	6.4	38	0.19

$[NH_3+NH_4^+]$ = 120 mM, $[Na_2S_2O_3]$ = 20 mM, pH = 9.5, $[O_2]$ = 0.25 mM.

4.4 Dissolution of gold by copper(II)-ammonia-thiosulfate under nitrogen

4.4.1 Gold and platinum electrode potentials

Figure 4.7 shows the typical variation of gold dissolution with time, measured in two solutions that contained different concentrations of reagents. Fig. 4.8 shows that at a given copper(II) concentration, both gold and platinum electrodes gave the same potential readings. While both gold (E_{Au}) and platinum (E_{Pt}) electrode potentials decreased with time, the measured potential in a solution of lower initial concentrations of reagents (solution A) reached an equilibrium value close to 0.25 V after 2 hours (Fig. 4.8). The values of gold (E_{Au}) and platinum (E_{Pt}) electrode potentials in solution B continued to decrease and reached an equilibrium value of about 0.18 V after 6 hours.



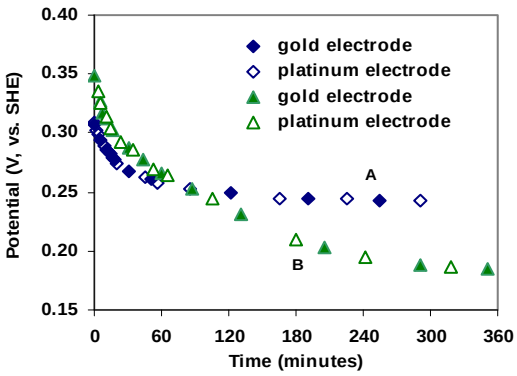


Fig. 4.7 *Effect of main reagents on gold dissolution in copper(II)-ammonia-thiosulfate solutions.*

Fig. 4.8 *Effect of main reagents on gold and platinum electrode potentials in copper(II)-ammonia-thiosulfate solutions.*
A: 0.3 mM Cu(II), 10 mM $Na_2S_2O_3$*, 60 mM* $NH_3 + NH_4^+$ *at pH 9.5.*
B: 1.5 mM Cu(II), 50 mM $Na_2S_2O_3$*, 240 mM* $NH_3 + NH_4^+$ *at pH 9.3.*

4.4.2 Effect of concentration of gold colloid

The effects of initial concentrations of gold colloid in the range of 0.03 mM to 0.15 mM on gold dissolution were also investigated. The results summarised in Appendix A 4.7 and Table 4.5 show a comparison between the dissolution and potential of gold. The extent of gold dissolution was larger at lower concentrations of gold colloid.

Table 4.5 *Effect of colloid strength on the dissolution and potentials of gold*

[Au(c)] mM	Gold dissolution (%)		Gold electrode potential (V) 180 min.
	10 min.	120 min.	
0.03	43.6	100	0.225
0.06	36.0	96	0.223
0.10	33.7	96	0.220
0.15	30.0	93	0.215

[Cu(II)] = 2.0 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.

4.4.3 Effect of particle size of gold colloid

Both stabilized colloids of average diameters 16, 25 and 30 nm, and unstabilized colloids of average diameters 12 nm and 32 nm, were used to investigate the effect of particle size on gold dissolution. Results are summarised in Appendices A 4.8 - 4.9. The decrease in concentration of copper(II) and potential of platinum electrode (E_{Pt}) measured in the absence of gold colloid in these reactions are shown in Appendix A 4.10. Table 4.6 summarises the effect of particle size on the dissolution and potentials of gold.

Colloids with smaller particle size dissolved faster. After 180 minutes, the final extent of dissolution was approximately the same (about 90%). The unstabilized colloid reacted faster (76% at 12 nm compared with stabilized colloid 22% at 16 nm) in the first 10 minutes. The gold potentials in all cases reached the same value of 0.245 V after 180 minutes.

Table 4.6 *Effect of colloid particle size on the dissolution and potentials of gold*

Gold particle size (nm)	Gold dissolution (%)			Gold electrode potential (V)
	10 min.	60 min.	180 min.	180 min.
Stabilized (16)	22	79	88	0.244
Stabilized (25)	18	62	90	0.245
Stabilized (30)	17	56	91	0.245
Unstabilized (12)	76	89	92	0.247
Unstabilized (32)	18	66	92	0.243

$[Cu(II)_i]$ = 1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 0.12 M, pH = 9.5.

4.4.4 Effect of ionic strength

Appendix A 4.11 shows the dissolution and potential of gold as a function of time in solutions of different ionic strengths (I = 0.2, 0.5, 1.0) adjusted using sodium sulfate. As shown in Table 4.7, gold dissolution in the first 10 minutes was nearly doubled when the ionic strength was increased from 0.2 to 1.0. The dissolution of gold after 360 minutes was also increased (from 69% to 78%), but the potential of gold (E_{Au}) was relatively unchanged as shown in Appendix A 4.11 and Table 4.7. The residual concentration of copper(II) in solution and platinum electrode potentials (E_{Pt}) increased with increasing ionic strength

(Appendix A 4.11). Therefore, higher residual concentration of copper(II) at higher ionic strength appeared to be the reason for the greater extent of gold dissolution shown in Table 4.7.

Table 4.7 *Effect of ionic strength on the dissolution and potentials of gold*

Ionic strength	Gold dissolution (%)		Gold electrode potential (V) 360 min.
	10 min.	360 min.	
0.2	7	69	0.245
0.5	9	74	0.257
1.0	13	78	0.257

[Cu(II)] = 1.5 mM, [$Na_2S_2O_3$] = 10 mM, [NH_3+NH_4^+] = 60 mM, pH = 9.5.

Based on the results summarized in Sections 4.3.2 - 4.3.4, the following conditions were selected for further investigation of the kinetics of gold dissolution with respect to pH, concentration of copper(II), thiosulfate, ammonia, temperature, and the presence of other salts such as $AgNO_3$, $Pb(NO_3)_2$, $NaNO_3$, $Na_2S_4O_6$, $Na_2S_3O_6$, Na_2SO_3 and Na_2CO_3.

- Diameter of gold colloid particles : 20 nm.
- Gold colloid concentration : 0.1 mM.
- Ionic strength in solution : 0.5 (Na_2SO_4).

4.4.5 Effect of copper(II) concentration

Han (2001) demonstrated the use of Cu(II)-NH_3-O_2 lixiviants at high temperature and oxygen pressures for leaching gold from a refractory sulfide ore. Therefore, in the present study, the effect of copper(II) and ammonia on the oxidation of gold colloid was investigated in the presence or absence of

thiosulfate. Appendices A 4.12 - A 4.13 and Table 4.8 show the dissolution and potential of gold as a function of time in the presence or absence of thiosulfate at different concentrations of copper(II). In the absence of thiosulfate, copper(II)-ammonia can react with gold. However, the increase in concentrations of copper(II) (0.5 mM – 2.5 mM) had no significant effect on the oxidation of gold. Only 2% and 8% to 12% of gold was dissolved after 10 minutes and 300 minutes respectively in the absence of thiosulfate (Table 4.8).

In the presence of thiosulfate, an increase in the concentration of copper(II) had a positive effect on gold dissolution as shown in Appendix A 4.13 and Table 4.8. The fraction proportion of gold dissolved after 10 minutes and 300 minutes varied between 15% to 42% and 60% to 98% respectively, with the increase in initial concentration of copper(II) from 0.5 mM to 4.5 mM. Without thiosulfate a solution of 0.5 mM copper(II) dissolved only 2% and 8% of gold after 10 minutes and 300 minutes respectively. The gold dissolution increased to 15% and 60% in the presence of thiosulfate.

Without thiosulfate, gold electrode potential increased from 0.22 V to 0.28 V with an increase of concentration of copper(II). However, the potential remained relatively unchanged at 0.18 V - 0.19 V (Table 4.8) in the presence of thiosulfate. The concentration of copper(II) decreased faster at higher initial concentrations. All concentrations reached constant values after 2 hours (Appendix A 4.13), while a higher initial concentration of copper(II) lead to a relatively higher final concentration of copper(II).

Table 4.8 *Effect of copper(II) on the dissolution and potentials of gold*

[Cu(II)] mM	[NH_3+NH_4^+] mM	[$Na_2S_2O_3$] mM	pH	Gold dissolution (%)		E_{Au} (V) 360 min.
				10 min	300 min	
0.5	120	0	9.5	2	8	0.22
2.5				2	12	0.28
0.5	240	50	9.3	15	60	0.18
4.5				42	98	0.19

4.4.6 Effect of thiosulfate concentration

Appendix A 4.14 shows gold dissolution, gold electrode potential, residual copper(II) concentration, and platinum electrode potential during the dissolution of gold at different initial concentrations of sodium thiosulfate. Table 4.9 shows the positive effect of higher thiosulfate concentrations on gold dissolution in the first 10 minutes. However, the overall gold dissolution after 5 hours decreased from 97% to 61% with the increase in initial concentration of thiosulfate from 20 mM to 95 mM. This also increased the initial (< 1 minute) gold electrode potential (Table 4.9). An opposite trend was observed after 300 minutes, when the gold electrode potential decreased from 0.230 V to 0.142 V with increasing concentration of thiosulfate.

The concentration of residual copper(II) decreased with increasing concentration of thiosulfate, as shown in Appendix A 4.14. In solutions of 10 mM thiosulfate, the concentration of copper(II) decreased from 1.50 mM to 1.05 mM, but a larger decrease to 0.05 mM was observed in 95 mM thiosulfate. This was also evident from the platinum electrode potential, which decreased from

0.250 V to 0.170 V with the increase in initial concentration of thiosulfate from 10 mM to 95 mM (Appendix A 4.14).

Table 4.9 *Effect of thiosulfate on the dissolution and potentials of gold*

$[S_2O_3^{2-}]$ mM	Gold dissolution (%)		Gold electrode potential (V)	
	10 min.	300 min.	< 1 min.	300 min.
10	10.8	92	0.299	0.230
20	15.1	97	0.321	0.220
30	18.3	92	0.333	0.220
50	20.5	88	0.348	0.187
70	20.2	83	0.363	0.178
95	22.5	61	0.369	0.142

[Cu(II)] = 1.5 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.3, Ionic strength 0.5.

4.4.7 Effect of ammonia concentration

Appendix A 4.15 and Table 4.10 show that the effect of an increase in concentration of ammonia on gold dissolution was insignificant in the absence of thiosulfate. Only 2% to 3% and 7% to 9% of gold was dissolved in the first 10 minutes and after 6 hours respectively, at pH 9.5. In the presence of thiosulfate, gold dissolution increased from 5% to 15% (after 10 minutes), and from 74% to 96% (after 5 hours) when the total concentration of ammonia was increased from 60 mM to 240 mM (Table 4.10). However, ammonia concentrations higher than 240 mM caused no further increase in gold dissolution (Appendix A 4.16).

In the absence of thiosulfate, the gold electrode potential increased and reached stable values after 5 hours (0.22 V - 0.27 V). The potentials were lower in the presence of thiosulfate (0.19 V - 0.24 V after 5 hours, Table 4.10).

Table 4.10 *Effect of ammonia on the dissolution and potentials of gold*

$[NH_3 + NH_4^+]$ mM	$[Na_2S_2O_3]$ mM	pH	Gold dissolution (%)		Gold electrode potential (V) after 5 hrs.
			10 min.	5 hrs.	
60 - 240	0	9.5	2-3	7 - 9	0.22 - 0.27
50 - 580	20	9.3	5-15	74 - 96	0.19- 0.24

[Cu(II)] = 1.5 mM, Ionic strength 0.5.

Appendix A 4.16 shows residual copper(II) concentrations and platinum electrode potentials versus time at different initial ammonia concentrations, while Table 4.11 highlights the main trends. The platinum electrode potential and residual copper(II) concentration were higher at higher initial concentrations of ammonia. This indicates that higher ammonia concentrations retarded the rate of degradation of thiosulfate and thus retained more copper(II) in solution due to the stabilisation of $Cu(NH_3)_4^{2+}$ complexes.

Table 4.11 *Effect of ammonia on the residual copper(II) and potentials of platinum electrode*

$[NH_3 + NH_4^+]$ mM	[Cu(II)] mM initial	[Cu(II)] mM 1 hr.	[Cu(II)] mM 5 hrs.	E_{Pt} (V) 5 hrs.
50	1.5	0.15	0.1	0.219
240	1.5	1.25	0.75	0.247
580	1.5	1.4	1.2	0.250

$[Na_2S_2O_3]$ = 20 mM, pH = 9.3.

4.4.8 Effect of pH

Appendix A 4.17 and Table 4.12 summarise the positive effect of increasing pH on the rate of gold dissolution. An increase in pH from 8.9 to 11.0 increased gold dissolution. The initial decrease in gold electrode potentials was also larger at high pH, but the overall decrease in potential was greater at lower pH.

Table 4.12 *Effect of pH on the dissolution and potentials of gold*

pH	Gold dissolution (%)		E_{Au} (V)
	10 min.	150 min.	0 min. - 150 min.
8.9	15	65	0.406 - 0.162
11.0	23	94	0.34 - 0.246

[Cu(II)] = 2.0 mM, $[Na_2S_2O_3]$ = 40 mM, $[NH_3+NH_4^+]$ = 240 mM.
(Appendix A 4.17).

Appendix A 4.17 and Table 4.13 show the change in concentration of residual copper(II) and platinum electrode potential during reaction. Higher values of pH retarded the reaction of copper(II) with thiosulfate. For example, the concentration of copper(II) decreased from 2.0 mM to 0.46 mM after 10 minutes and to 0.14 mM after 150 minutes at pH 8.9. However, at pH 11, the decrease was from 2.0 mM to 1.83 mM after 150 minutes. The platinum electrode potentials remained higher at higher values of pH (Table 4.13).

Table 4.13 *Effect of pH on residual copper(II) concentration and platinum electrode potentials*

pH	[Cu(II)] (mM)			E_{Pt} (V)
	0 min.	10 min.	150 min.	150 min.
8.9	2.0	0.46	0.14	0.217
11.0	2.0	1.99	1.83	0.272

$[Na_2S_2O_3]$ = 40 mM, $[NH_3+NH_4^+]$ = 240 mM.

4.4.9 Effect of concentrations of sodium nitrate and silver nitrate

Appendix A 4.18 and Table 4.14 show that sodium nitrate in the concentration range 0 M to 0.33 M had no significant effect on the dissolution and potential of gold. Likewise, copper (II) concentration and platinum electrode potential remained relatively unchanged during the reaction, despite the change in concentration of sodium nitrate from 0 M to 0.1 M.

Table 4.14 *Effect of nitrate on the dissolution and potentials of gold*

$[NaNO_3]$ mM	Gold dissolution (%)		E_{Au} (V)
	10 min.	5 hrs.	5 hrs.
0	12	96	0.233
0.33	14.5	98	0.244

[Cu(II)] = 1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH = 9.5.

Jeffrey et al. (2001b) showed that the oxidation of gold in CN^--O_2 and Cu(II)-NH_3-$S_2O_3^{2-}$ system was catalysed by alloyed silver. Webster (1986) found that gold dissolution in O_2-$S_2O_3^{2-}$ system was increased by the presence of silver-thiosulfate complexes or alloyed silver. In the present study, the effect of silver(I) on the dissolution of gold colloid in Cu(II)-NH_3-$S_2O_3^{2-}$ was investigated by adding silver nitrate of different concentrations. Since the nitrate anion had a

negligible effect (Table 4.14) it was possible to investigate the specific effect of Ag(I) on gold dissolution by investigating the effect of dissolved $AgNO_3$.

Appendix A 4.19 and Table 4.15 show that the increase in concentration of silver(I) ions from 0 mM to 0.15 mM caused an increase in gold dissolution from 12% to 35% (after 10 minutes), 43% to 96% (after 60 minutes) and 96% to 99% (after 300 minutes). Silver(I) ions slightly increased the gold electrode potential partly due to the increase in concentration of gold(I). The presence of silver(I) ions caused a rapid decrease in the concentration of copper(II) in the first 40 minutes, but the subsequent decrease was slower (Appendix A 4.19). Therefore, the final platinum electrode potentials were 20 mV - 25 mV higher in the presence of silver ions.

Table 4.15 *Effect of silver(I) on the dissolution and potentials of gold*

$[AgNO_3]$ mM	Gold dissolution (%)			E_{Au} potential (V)
	10 min.	60 min.	300 min.	300 min.
0	12	43	96	0.230
0.15	35	96	99	0.247

[Cu(II)] = 1.5 mM, $[NH_3+NH_4^+]$ = 0.12 M, $[Na_2S_2O_3]$ = 20 mM, pH = 9.5.

4.4.10 Effect of silver colloid

Webster (1986) reported that silver colloid or silver alloy could improve gold colloid dissolution. Thus, some experiments were performed in the presence of both copper(II) and silver colloid under nitrogen. Figs. 4.9-4.10 and Table 4.16

compare the dissolution of gold colloid and silver colloid in copper(II)-ammonia-thiosulfate solution. It should be noted that:

(i) The dissolution of silver colloid was faster than that of gold colloid.

(ii) The addition of silver nitrate showed a large positive effect on the dissolution of gold colloid (Fig. 4.10).

(iii) The addition of silver nitrate increased the residual concentration of copper(II) in the first 45 minutes; but in later stages the residual concentration of copper(II) was lower in the presence of silver nitrate (Appendix A 4.20).

(iv) The platinum electrode potentials in the presence of silver nitrate or silver colloids show similar trends to gold potentials (Appendix A 4.20).

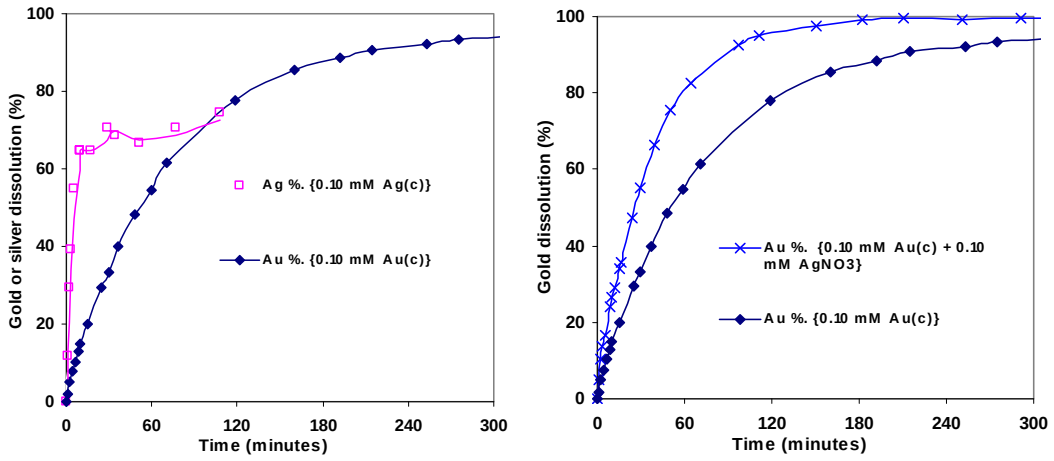


Fig. 4.9 *The dissolution of gold and silver colloid in copper(II)-ammonia-thiosulfate solutions.*

Fig. 4.10 *Effect of silver nitrate on gold dissolution in copper(II)-ammonia-thiosulfate solutions.*
[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+ NH_4^+] = 120 mM, pH = 9.5.

Table 4.16 *The dissolution of gold and silver colloids in copper(II)-ammonia-thiosulfate solutions*

Colloid / additive	Gold dissolution (%)		Silver dissolution (%)		E_{Au} (V)
	10 min.	4 hrs.	10 min.	4 hrs.	5 hrs.
Ag colloid	-	-	65		-
Au colloid	15	91	-		0.238
Au colloid + $AgNO_3$	27	99	-		0.249

$[CuSO_4]$ = 1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3 + NH_4^+]$ = 120 mM, [Ag(c)] = 0.1 mM, pH = 9.5.

4.4.11 Effect of lead nitrate

As shown in Appendix A 4.21 and Table 4.17 the addition of 0.01 mM lead(II) resulted in a decrease in gold dissolution, while the same concentration of Ag(I) gave a positive effect. The presence of lead(II) ions showed no significant effect on the residual concentration of copper(II) nor the electrode potential of gold and platinum in the later stages (Appendix A 4.21).

Table 4.17 *Effects of lead(II) and silver(I) on the dissolution and potentials of gold*

Additive mM	Gold dissolution (%)			E_{Au} (V)
	10 min.	120 min.	300 min.	300 min.
no additive	12	73	97	0.23
$Pb(NO_3)_2$ (0.01mM)	11	68	93	0.24
$AgNO_3$ (0.01mM)	15	78	97	0.24

[Cu(II)] = 1.5 mM, $[NH_3+NH_4^+]$ = 120 mM, $[Na_2S_2O_3]$ = 20 mM, pH = 9.5.

4.4.12 Effect of sodium chloride

The process water used in most gold plants contains chloride and there is evidence for the formation of mixed Cu(I)-Cl^--$S_2O_3^{2-}$ complexes (Black et al., 2003). Therefore, the effect of adding NaCl at concentrations up to 0.33 M was investigated, in the absence or presence of thiosulfate.

(a) Effect of chloride ions in the absence of thiosulfate

Appendix A 4.22 and Table 4.18 show the effect of chloride ions in the system Au(c)-Cu(II)-NH_3. There was no significant improvement in gold dissolution caused by chloride ions in the initial 10 minutes (3% - 5%) and after 300 minutes (13% - 14%) . The effect of chloride on gold electrode potentials was complex (Appendix A 4.22), However, the effect of chloride on final gold electrode potential (0.26 V after 6 hours) was negligible (Table 4.18). Moreover, the residual concentration of copper(II) was also unaffected by chloride (Appendix A 4.22) in the absence of thiosulfate.

Table 4.18 *Effect of chloride on the dissolution and potentials of gold in the absence of thiosulfate*

[NaCl] M	[NH_3 + NH_4^+] mM	[$Na_2S_2O_3$] mM	Gold dissolution (%)		E_{Au} potential (V)
			10 min.	300 min.	300 min.
0	120	0	3	13	0.26
0.10	120	0	5	14	0.26
0.33	120	0	5	14	0.26

[Cu(II)] = 1.5 mM, pH = 9.5.

(b) Effect of chloride ions in the presence of thiosulfate

Appendix A 4.23 and Table 4.19 show the effect of chloride ions in the system Au(c)-Cu(II)-NH_3-$S_2O_3^{2-}$. In the presence of thiosulfate, chloride ions showed a positive effect on gold dissolution, with an increase in gold dissolution after 10 minutes and 5 hours from 10% to 22% and from 92% to nearly 100 % respectively (Table 4.19). However, the gold potentials and residual concentration of copper(II) were unaffected by the presence of chloride (Appendix A 4.23).

Table 4.19 *Effect of chloride on the dissolution and potentials of gold in the presence of thiosulfate*

[NaCl] M	[NH_3 + NH_4^+] mM	[$Na_2S_2O_3$] mM	Gold dissolution (%)		E_{Au} potential (V)
			10 min.	300 min.	300 min.
0	120	20	10	92	0.23
0.10	120	20	18	99	0.24
0.33	120	20	22	99.5	0.24

[Cu(II)] = 1.5 mM, pH = 9.5.

4.4.13 Effect of carbonate, trithionate, tetrathionate, and sulfite

Appendix A 4.24 and Table 4.20 show the effect of $Na_2S_3O_6$, $Na_2S_4O_6$, Na_2CO_3, and Na_2SO_3 on the dissolution and potentials of gold. Results show a small positive effect of $Na_2S_3O_6$ on the rate of gold dissolution during the first 2 hours, but $Na_2S_4O_6$ showed a small negative effect. Both Na_2SO_3 and Na_2CO_3 also showed negative effects. The gold dissolution after 5 hours (Table 4.20) showed that the detrimental effect of Na_2SO_3 was greater than that of Na_2CO_3.

For example, the gold dissolution after 5 hours was decreased by 5% in the presence of carbonate, by 11% to 12% in the presence of trithionate and tetrathionate, and by 75% in the presence of sulfite (Table 4.20).

Table 4.20 *Effect of different anions on the dissolution and potentials of gold and residual copper(II)*

Additive (mM)	Gold dissolution (%).			E_{Au} (V)	Cu(II) (mM)
	10 min.	120 min.	300 min.	300 min.	120 min.
no additive	12	77	97	0.23	0.82
Na_2CO_3 (110)	8.5	47	92	0.22	1.32
$Na_2S_3O_6$ (20)	13.4	79	85	0.24	0.71
$Na_2S_4O_6$ (5)	11	72	86	0.20	0.58
Na_2SO_3 (40)	2.6	14.5	22	0.16	0.50

[Cu(II)] = 1.5 mM, $[NH_3+NH_4^+]$ = 120 mM, $[Na_2S_2O_3]$ = 20 mM, pH = 9.5.

A comparison of the results shown in Table 4.20 and Appendix. A4.24 reveals that the initial (120 min.) decrease in residual concentration of copper(II) caused by the reaction between copper(II) and thiosulfate was enhanced in the presence of sulfite > tetrathionate > trithionate, but retarded in the presence of carbonate. The decrease in platinum electrode potentials shown in Appendix A 4.24 was consistent with the change in concentration of copper(II). Although the residual concentration of copper(II) and the platinum electrode potential in the presence of Na_2CO_3 remained higher, the gold dissolution was lower during the first 3 hours. However, the final gold dissolution in the presence of carbonate was the highest among measurements made in the presence of the various salts tested (Table 4.20 and Appendix. A4.24).

4.4.14 Effect of temperature

Appendix A 4.25 and Table 4.21 summarise the effect of temperature on the dissolution and potentials of gold. Gold dissolution in the first 10 minutes increased from 23% at 22ºC to 77% at 48ºC (Table 4.21). The gold electrode potential showed a decrease, which was larger at high temperatures than that at low temperatures.

The reduction of copper(II) by thiosulfate also appeared to occur more rapidly at high temperatures. For example, after 180 minutes, the concentration of copper(II) decreased from 2 mM to 0.55 mM at 22°C, but to 0.26 mM at 48ºC. Platinum electrode potentials in blank solution (in the absence of gold colloid) also decreased with increasing temperature, from about 0.35 V to 0.24 V (22ºC), and to 0.10 V (48ºC) after 180 minutes as a result of the decrease in copper(II) concentration (Appendix A 4.25).

Table 4.21 *Effect of temperature on the dissolution and potentials of gold and residual copper(II)*

T (ºC)	Gold dissolution (%)			E_{Au} (V)	Cu(II) (mM)
	10 min.	60 min.	180 min.	180 min.	180 min.
22	23	55	83	0.236	0.55
30	35	75	98	0.205	0.43
40	60	97	98	0.170	0.40
48	77	97	98	0.141	0.26

[Cu(II)] = 2.0 mM, $[NH_3+NH_4^+]$ = 240 mM, $[Na_2S_2O_3]$ = 50 mM, pH = 9.5.

4.5 Dissolution of gold in thiosulfate solutions by oxygenated copper(II)

4.5.1 Effect of oxygen concentration

Figure 4.11 and Table 4.22 summarise the results from experiments performed at different oxygen concentrations. In the first 10 minutes, the gold dissolution (32% - 36%) was nearly the same for all oxygen concentrations (Table 4.22). Gold dissolution in the absence of oxygen (under nitrogen) after 100 minutes was slightly higher (68%) than that with oxygen (62%). Gold dissolution in oxygen bubbled solutions ceased at 64% after 180 minutes (Fig. 4.11), but increased to 82% without oxygen or at lower oxygen concentrations (open to air).

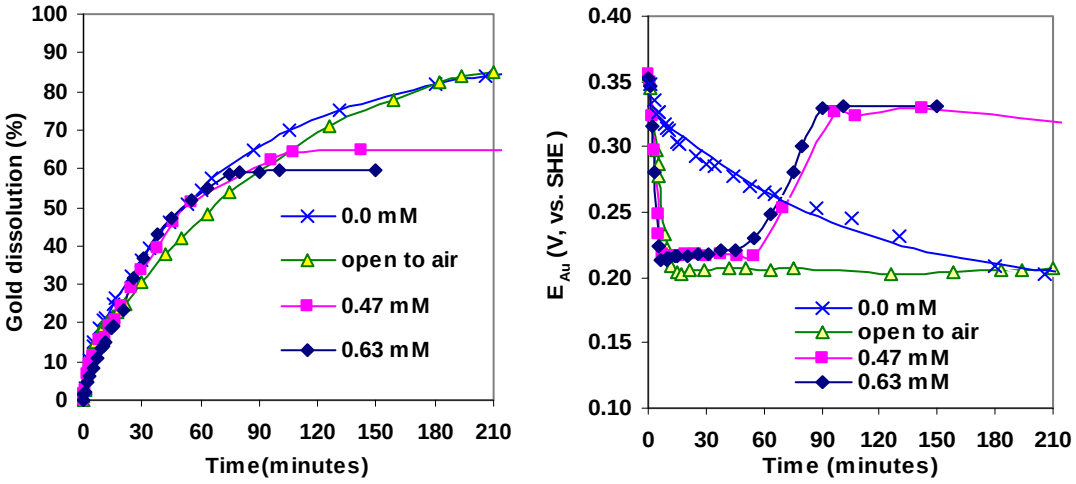


Fig. 4.11 *Effect of oxygen on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. 4.12 *Effect of oxygen on electrode potential in copper(II)-ammonia-thiosulfate solution.*
Conditions: $[CuSO_4]$ = 1.5 mM, $[Na_2S_2O_3]$ = 50 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.5.

Table 4.22 *Effect of oxygen on gold dissolution in oxygenated copper(II)-ammonia-thiosulfate solution*

$[O_2]$ mM	Gold dissolution (%)		
	10 min.	100 min.	180 min.
0	36	68	82
0.06 – 0.25*	31	62	82
0.47	33	62	64
0.63	36	62	64

$[CuSO_4]$ = 1.5 mM, $[Na_2S_2O_3]$ = 50 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.5.

* Open to air.

Figure 4.12 shows the variation of gold electrode potential in Cu(II)-Au(c)-NH_3-$S_2O_3^{2-}$ solution while Figs. 4.13-4.14 show the residual copper(II) concentration and platinum electrode potential in Cu(II)-NH_3-$S_2O_3^{2-}$ solutions exposed to different oxygen concentrations. Figs. 4.15 and 4.16 show the potential versus time curves to show similar trends in the gold (E_{Au}) and platinum (E_{Pt}) electrode potential in most cases, thus suggesting that both electrodes measure the same redox couple Cu(II)/Cu(I) (or the mixed potential) under these conditions.

The large decrease in gold (E_{Au}) and platinum (E_{Pt}) electrode potential in the presence of oxygen or air compared to that in the absence of oxygen (Figs. 4.15, 4.16) indicates a faster reaction between copper(II) and thiosulfate in the presence of oxygen. This is consistent with the results reported by Breuer and Jeffrey (2003a). In both cases the potential remained low and constant at about 0.2 V when air was used as the oxygen source (Fig. 4.15). However, in solutions of higher oxygen concentration, the values of platinum electrode potential (E_{Pt}) showed a rapid decrease in Fig. 4.16, followed by an increase

after 80 minutes (at 0.47 mM O_2) or 60 minutes (at 0.63 mM O_2). This suggests the oxidation of copper (I) to copper (II), a view supported by the increase in concentration of copper(II) shown in Fig. 4.13. Moreover, the time independent E_{Pt} of 0.23 V, 0.22 V and 0.21 V at the three different concentrations of oxygen in Fig. 4.14 are in the range of Eh predicted for the $Cu(NH_3)_4^{2+}/Cu(S_2O_3)_2^{3-}$ couple (Eh-pH diagram shown in Fig. 2.1).

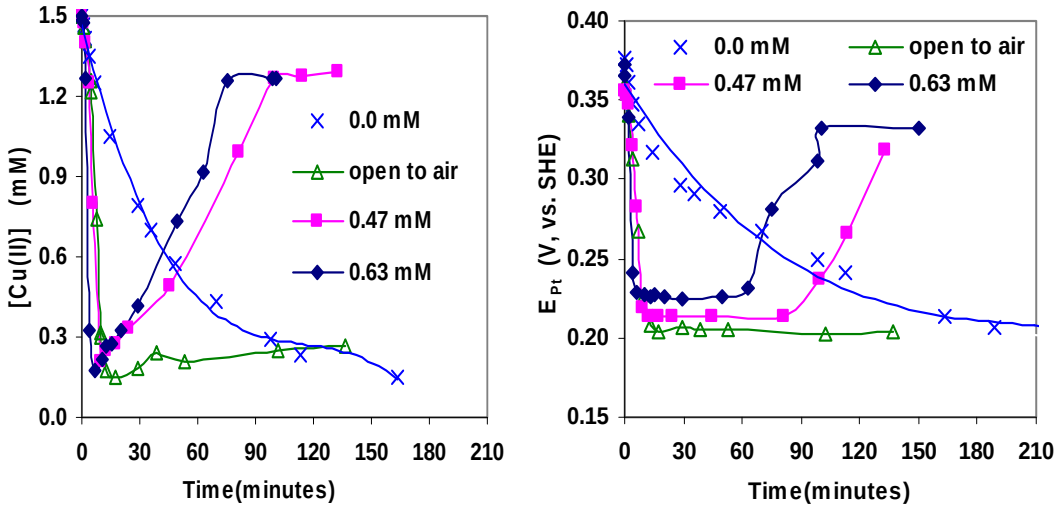


Fig. 4.13 *Effect of oxygen on residual copper(II) concentration in copper(II)-ammonia-thiosulfate solutions.*

Fig. 4.14 *Effect of oxygen on platinum electrode potential in copper(II)-ammonia-thiosulfate solutions.*

$[CuSO_4]$ = 1.5 mM, $[Na_2S_2O_3]$ = 50 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.5.

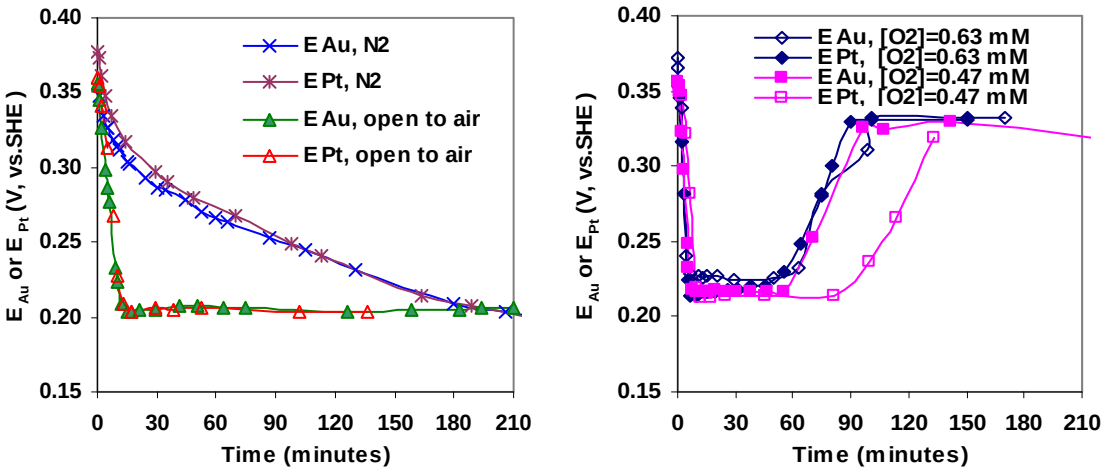


Fig. 4.15 *Comparison of gold and platinum electrode potentials in copper(II)-ammonia-thiosulfate solutions.*

Fig. 4.16 *Comparison of gold and platinum electrode potentials in oxygenated copper(II)-ammonia-thiosulfate solutions. [$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.*

4.5.2 Effect of copper(II) concentration

Appendix A 4.26 and Table 4.23 show the gold dissolution at different concentrations of copper(II) (1.0 mM - 3.0 mM) in solutions of 0.31 mM dissolved oxygen. In the first hour, gold dissolution increased with increasing concentration of copper(II). There was an increase from 13% to 28% in 10 minutes, 40% to 85% in 60 minutes, and 83% to 92% in 200 minutes (Table 4.23). Due to the side reaction of copper(II) with thiosulfate, a high initial concentration of copper(II) caused the consumption of more copper(II) and thiosulfate. Thus, depending on the initial concentration of copper(II), gold

dissolution ceased after 1.5 hours (3.0 mM copper(II)), 2 hours (2.0 mM copper(II)), and 3.5 hours (1.0 mM copper(II)) (Appendix A 4.26).

The effect of increasing the initial concentration of copper(II) on gold (E_{Au}) and platinum (E_{Pt}) electrode potential and residual concentration of copper(II) was similar to that of increasing oxygen concentration described previously. Higher values of potential were generally associated with higher concentrations of copper(II). This in turn gave higher gold dissolution in the first 60 minutes (Table 4.23 and Appendix Fig. A4.26).

Table 4.23 *Effect of copper(II) concentration on gold dissolution in oxygenated copper(II)-ammonia-thiosulfate solution*

[Cu(II)] mM	Gold dissolution (%)		
	10 min.	60 min.	200 min.
1.0	13	40	83
2.0	16	67	91
3.0	28	85	92

$[O_2]$ = 0.31 mM, $[Na_2S_2O_3]$ = 50 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.3.

4.5.3 Effect of thiosulfate concentration

Appendix A 4.27 and Table 4.24 show the effect of thiosulfate concentration on the extent of gold dissolution. In the initial 6 minutes, gold dissolution decreased with increasing concentration of thiosulfate (Table 4.24). After 45 minutes, higher concentrations of thiosulfate led to higher gold dissolution and the results at 60 minutes confirmed this trend. The gold dissolution reached 92% in 2 hours in 50 mM thiosulfate solution, but ceased at 60% and 35% dissolution in

solutions of 30 mM and 20 mM thiosulfate, respectively, after 1.5 hours (Table 4.24 and Appendix A 4.27).

The change in gold (E_{Au}) and platinum (E_{Pt}) electrode potential and residual concentration of copper(II) with increasing concentrations of thiosulfate (Appendix A 4.27) showed an effect opposite to that caused by increasing concentrations of copper(II) or oxygen described in previous sections. For example, high concentrations of thiosulfate resulted in lower residual copper(II) and lower platinum electrode potentials.

Table 4.24 *Effect of thiosulfate on gold dissolution in oxygenated copper(II)-ammonia-thiosulfate solution*

$[Na_2S_2O_3]$ mM	Gold dissolution (%)		
	6 min.	60 min.	120 min.
20	19	34	35
30	16	57	60
50	12	67	92

$[O_2]$ = 0.31 mM, [Cu(II)] = 2.0 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.3.

4.6 Dissolution of gold powder in thiosulfate solutions under nitrogen

4.6.1 Effect of copper(II) concentration

Figures 4.17-4.18 and Table 4.25 show the extent of dissolution and the electrode potential of gold as a function of time in solutions with different concentrations of copper(II). The extent of gold dissolution varied between 5.5% to 8.6% and 24% to 31% after 1 hour and 7 hours respectively. These values are much lower than the 85% to 95% dissolution of gold colloid achieved after 7 hours. However, the gold electrode potential remained the same at approximately 0.22 V - 0.23 V over 6 hours in all cases (Table 4.25).

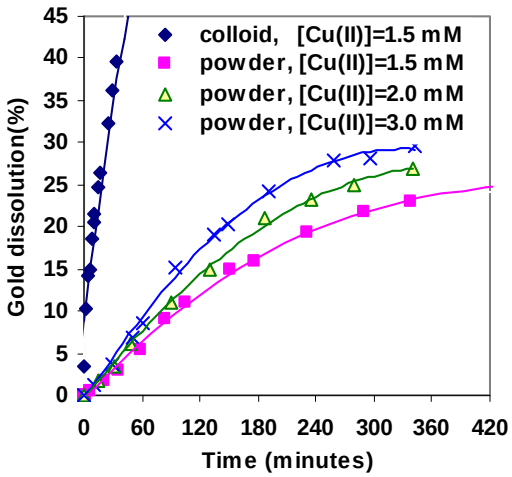
Table 4.25 *Effect of initial copper(II) on the dissolution of gold colloid, gold powder, and gold electrode potentials*

[Cu(II)] mM	Gold dissolution (%)		E_{Au} (V)
	1 hr.	7 hrs.	6 hrs.
1.5	5.5	24	0.223
2.0	7.5	28	0.223
3.0	8.6	31	0.224
1.5*	54	89	0.228

$[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH = 9.5, $[O_2]$ = 0 mM.
Gold powder particle size: 1.5 µm - 3.0 µm. * 0.1 mM gold colloid (20 nm).

Figure 4.19 shows the change of concentrations of copper(II) in Cu(II)-NH_3-$S_2O_3^{2-}$ solution during the dissolution of gold powder. It can be seen that the residual concentration of copper(II) decreases faster at the higher initial concentration. Fig. 4.19 also shows that the change in concentrations of

copper(II) in the absence of gold (line D) followed the same trend as that in the presence of gold powder (line A).



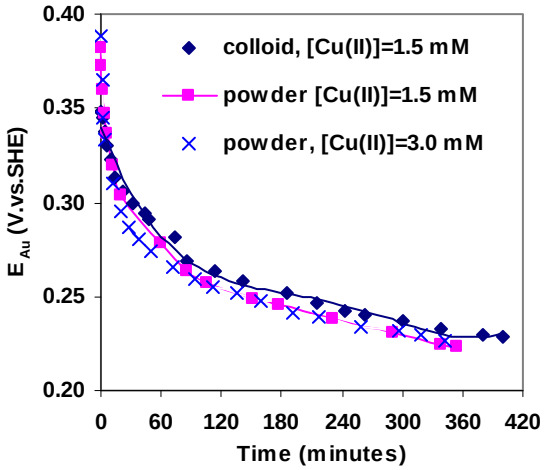


Fig. 4.17 *Effect of copper(II) on the dissolution of gold powder in copper(II)-ammonia-thiosulfate solution.*

Fig. 4.18 *Effect of copper(II) on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*

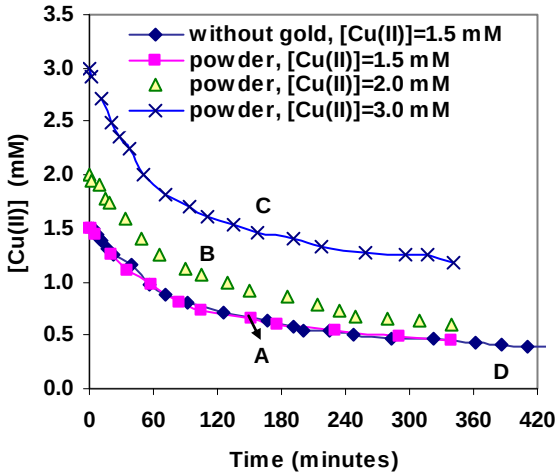


Fig. 4.19 *Change in residual copper(II) concentration during gold powder dissolution. [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.*

4.6.2 Effect of silver and chloride ions

Silver(I) and chloride ions both showed a catalytic effect and increased the rate of dissolution of gold colloids as described in previous sections. The same phenomenon was observed for the dissolution of gold powder (Appendix A 4.28 and Table 4.26). Without any additive, the percentage of gold powder dissolved in 1 hour and 7 hours was 6% and 24% respectively. In the presence of silver nitrate these values increased to 17% and 32% respectively. Comparable values of 13% and 36% were obtained in the presence of sodium chloride (Table 4.26). Appendix A 4.28 shows that gold electrode potentials, during the dissolution of gold powder, followed the same trend as in the dissolution of gold colloids, and reached a value of 0.23 V in 6 hours (Table 4.26). Appendix A 4.28 also shows that the residual concentrations of copper(II) were slightly increased in the presence of silver nitrate but decreased in the presence of sodium chloride.

Table 4.26 *Effect of silver and chloride ions on the dissolution of gold powder and gold electrode potentials*

Additive	Au powder dissolution (%)		E_{Au} (V)
	60 min.	7 hrs.	6 hrs.
No additive (powder)	6	24	0.223
0.05 mM $AgNO_3$ (powder)	17	32	0.235
100 mM NaCl (powder)	13	36	0.233
No additive (colloid)	54	89	0.232

$[CuSO_4]$=1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH = 9.5, $[O_2]$ = 0 mM.
Gold powder particle size: 1.5 µm - 3.0 µm, gold colloid particle size 20 nm.

4.6.3 Effect of particle size of gold powder

Commercial gold powders of two different size ranges (1.5 μm - 3.0 μm and 5.5 μm - 9.0 μm) were used to examine the effect of particle size on the rate of dissolution. The results summarised in Appendix A 4.29 and Table 4.27 show that the dissolution of gold powder after 60 minutes was only 6% and 4%. This is much less than that of gold colloid (56% to 78%) due to the low surface area. Gold electrode potentials and residual concentrations of copper(II) followed the same trend as observed in experiments with gold colloids.

Table 4.27 *A comparison of gold dissolution with different particle sizes.*

Particle size (nm) (average)	m^2/g	[Au(c)] (mM)	[Au(s)] (mM)	Gold dissolution (%) (60 min.)	
				gold colloid	gold powder
16	40	0.1		78	
25	26	0.1		62	
30	22	0.1		56	
2250	0.29		0.1		6
7250	0.089		0.1		4

[Cu(II)] = 1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH = 9.5.

CHAPTER 5 ELECTRODE POTENTIALS AND GOLD-COPPER SPECIATION

5.1 Introduction

Gold dissolution in ammoniacal thiosulfate solutions in the presence of oxygen and/or copper(II) is an electrochemical process in which the electrode potentials of the redox couples play important roles. The electrode potentials of the gold(I)/gold(0) and copper(II)/copper(I) couples are related to the nature of the chemical species involved in each redox couple. The complex chemistry of the oxidation of gold by the copper(II)/copper(I) redox couple is partly due to the fact that both ammonia and thiosulfate ligands form single-ligand or mixed-ligand complexes with gold(I), copper(I) and copper(II). The dissolution of gold by oxygen or copper(II) can be represented by the equations shown in Table 5.1. Some of these reactions may be involved in the rate controlling step.

Other complications arise due to the fact that both oxygen and copper(II) react with thiosulfate according to the equations presented in Chapter 2, while the oxidation products and host minerals can also interfere with gold dissolution. It is important to understand the nature of chemical speciation in order to formulate reaction mechanisms in different lixiviant systems. This chapter describes the analysis of gold(I), copper(I) and copper(II) speciation for different systems, based on the equilibrium concentrations of gold and the potentials of gold and platinum electrodes.

Table 5.1 *Possible chemical reactions involved in gold oxidation*

No.	Chemical reaction
	Basic redox reactions with oxygen or copper(II)
1.	$Au + 0.25O_2 + 0.5H_2O = Au^+ + OH^-$
2.	$Au + Cu^{2+} = Au^+ + Cu^+$
	Oxygenated ammonia, thiosulfate or mixed ammoniacal-thiosulfate system
3.	$Au + 0.25O_2 + 0.5H_2O = Au(OH)^0$
4.	$Au + 0.25O_2 + OH^- + 0.5H_2O = Au(OH)_2^-$
5.	$Au + 0.25O_2 + NH_3 + 0.5H_2O = Au(NH_3)(OH)^0$
6.	$Au + 0.25O_2 + 2NH_3 + 0.5H_2O = Au(NH_3)_2^+ + OH^-$
7.	$Au + 0.25O_2 + S_2O_3^{2-} + NH_3 + 0.5H_2O = Au(NH_3)(S_2O_3)^-$
8.	$Au + 0.25O_2 + 2S_2O_3^{2-} + 0.5H_2O = Au(S_2O_3)_2^{3-} + OH^-$
	Copper(II)-ammonia-thiosulfate systems
9.	$Au + Cu(NH_3)_m^{2+} = Au(NH_3)_2^+ + Cu(NH_3)_{m-2}^+$
10.	$Au + S_2O_3^{2-} + Cu(NH_3)_m^{2+} = Au(S_2O_3)(NH_3)^- + Cu(NH_3)_{m-1}^+$
11.	$Au + 2S_2O_3^{2-} + Cu(NH_3)_m^{2+} = Au(S_2O_3)_2^{3-} + Cu(NH_3)_p^+ + (m-p)NH_3$
12.	$Au + NH_3 + Cu(NH_3)_p(S_2O_3)^0 = Au(S_2O_3)(NH_3)^- + Cu(NH_3)_p^+$
13.	$Au + S_2O_3^{2-} + Cu(NH_3)_p(S_2O_3)^0 = Au(S_2O_3)_2^{3-} + Cu(NH_3)_p^+$

5.2 Relationship between electrode potentials, rates and speciation

As shown in Fig. 5.1, the rates of the anodic ($Au \rightarrow Au(I) + e^-$) and cathodic ($Cu(II) + e^- \rightarrow Cu(I)$) reaction rates per unit surface area (mol m^{-2} s^{-1}) can be represented by the respective current densities (A m^{-2}), where $E_{a(eq)}$ and $E_{c(eq)}$ represent equilibrium potentials of the anodic and cathodic reactions respectively. The potential at which the two rates become equal is defined as the mixed potential (E_{mix}). The relevant equations for the rate of dissolution at mixed potentials ($R = i_{mix}/nF$; n = number of electron, F = Faraday constant) have been recently reviewed by Pesic and Sergent (1993), and Nicol and Lazaro (2002).

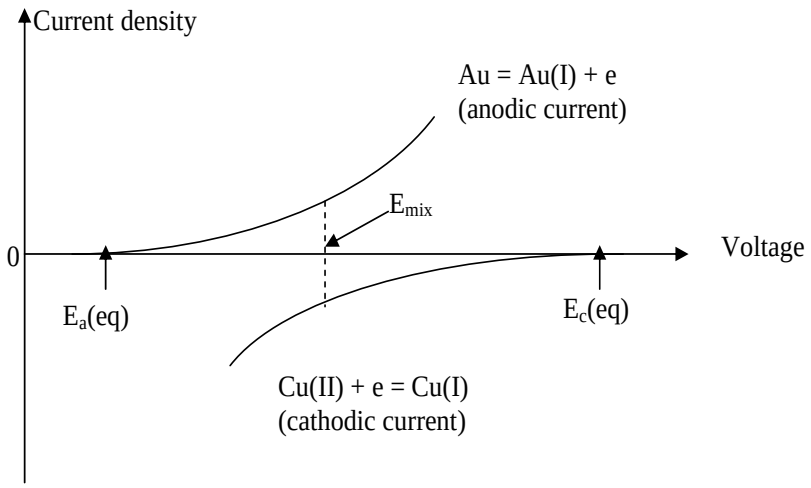


Fig. 5.1 *Schematic representation of current-potential curves for gold oxidation and copper(II) reduction.*

The oxidation of gold in thiosulfate solutions occurs according to Eq. 5.1. The standard reduction potential for this reaction is 0.153 V ($\beta_2=10^{26}$ used for

$Au(S_2O_3)_2^{3-}$) (Nicol et al., 1987; Hiskey and Atluri, 1988); and the recently reported value of $E^o\{Au(S_2O_3)_2^{3-}/Au(0)\}$ = 0.274 V is based on $\beta_2=10^{24}$ (Senanayake et al., 2003). The reduction of dissolved oxygen according to Eq. 5.2 has a standard potential of 0.401 V at pH 14 (Antelman and Harris, 1982), larger than that for Eq. 5.1 (Ec(eq) > Ea(eq)). Thus, dissolved oxygen should oxidise gold to its thiosulfate complex. However, this oxidation has been found to be very slow (Webster, 1986) due to the slow reduction of oxygen. Ritchie et al. (2001) confirmed this by calculating the rate of oxygen reduction using the current-potential relationship $i = 2.95 \times 10^{-7} \exp(-\eta/0.052)$ mA cm^{-2}, where η (= E_{mix}-E_e) is the overpotential for the reduction of oxygen. It was shown that the calculated rate of oxygen reduction from the current-potential relationship (6.2 x 10^{-8} mol m^{-2} s^{-1}) was three orders of magnitude lower than the calculated rate based on oxygen mass transfer to a suspended spherical 50 μm gold particle in an oxygen saturated solution (2.5 x 10^{-5} mol m^{-2} s^{-1}).

$$Au + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + e^- \quad (5.1)$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad (5.2)$$

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- = Cu(S_2O_3)_3^{5-} + 4NH_3 \quad (5.3)$$

In solutions containing copper(II), ammonia and thiosulfate, there is an additional cathodic reaction (Eq. 5.3) which has a standard potential of 0.22 V (Jeffrey, 2001). Moreover, Breuer and Jeffrey (2002) showed that the mixed potential 0.238 V in copper(II)-ammonia-thiosulfate solution is higher than that in oxygenated ammonia-thiosulfate solution, which is 0.065V, (also well below gold/thiosulfate couple). Ritchie et al. (2001) noted that it is possible to maintain a high copper(II)/copper(I) ratio due to the rapid oxidation of copper(I) ammines

by dissolved oxygen. This leads to higher values of E_c, E_{max} and i_{mix} in Fig. 5.1 and thus higher rates of oxidation of gold by the copper(II)/copper(I) redox couple, while acting as a redox-mediator in the presence of oxygen.

The E_H-pH diagrams provide useful information on redox as well as non-redox reactions involved in leach systems. However, as noted in Chapter 2, reliable E_H-pH diagrams for the ammoniacal-copper(II)/(I)-thiosulfate system, which includes all the soluble species, cannot be constructed. This is because the data on the mixed ligand complexes of copper(II)/(I) systems are unavailable. Nevertheless, the measured changes in potentials of gold and platinum electrodes and their relationship to chemical speciation can provide useful information which can be incorporated in rate analysis to rationalise reaction mechanisms.

Table 5.2 shows the effect of complex-formation with various ligands on the calculated standard reduction potentials E^o of the Au(I)/Au(0), Au(III)/Au(0) and Cu(II)/Cu(I) couples, assuming unit concentration of ligands and metal ions, and unit activity coefficients of all species. The calculated values in the present study closely agree with the reported values of $E^o_{Cu(II)/Cu(I)}$ (Aylmore and Muir, 2001a). The slight difference is a result of the different thermodynamic data used in the two cases.

Table 5.2 *Effect of complex-formation on standard reduction potentials at 25°C*

Reduction reaction	log β_n of complexes[a]			E^o / V [b]
	Au(I)	Au(III)	Cu(I)/Cu(II)[c]	Cu(II)/Cu(I) or Au(I)/Au(0)
$Au^+ + e = Au$				1.69
$Au^{3+} + 3e = Au$				1.50
$Cu^{2+} + e = Cu^+$				0.15
$Au(S_2O_3)_2^{3-} + e = Au + 2S_2O_3^{2-}$	24			0.27
$Au(NH_3)_2^+ + e = Au + 2NH_3$	19			0.56
$Au(NH_3)_4^{3+} + 3e = Au + 4NH_3$		59		0.33
$Cu(NH_3)_4^{2+} + e = Cu(NH_3)_2^+ + 2NH_3$			-2.42	0.06
$Cu(NH_3)_4^{2+} + 2S_2O_3^{2-} + e = Cu(S_2O_3)_2^{3-} + 4NH_3$			0.09	0.16(0.14)
$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e = Cu(S_2O_3)_3^{5-} + 4NH_3$			1.53	0.24(0.22)
$Cu(NH_3)_3^{2+} + 2S_2O_3^{2-} + e = Cu(S_2O_3)_2^{3-} + 3NH_3$			1.88	0.26(0.20)
$Cu(NH_3)_3^{2+} + 3S_2O_3^{2-} + e = Cu(S_2O_3)_3^{5-} + 3NH_3$			3.32	0.36(0.36)

a. Smith and Martell, 1976; Skibsted and Bjerrum, 1974; and Table 1.2.

b. Values in parentheses from Aylmore and Muir (2001a);
Concentration of ligand = metal complex = 1 M, unit activity coefficients $\gamma = 1$,
$E^o\{Au(I)/Au(0)\} = E^o\{Au^+/Au(0)\} - 0.059 \log \beta_n\{Au(I) \text{ complex}\}$,
$E^o\{Cu(II)/Cu(I)\}$
$= E^o\{Cu^{2+}/Cu^+\} - 0.059 [\{\log \beta_n\{Cu(I) \text{ complex}\} - \log \beta_n \{Cu(II) \text{ complex})\}]$.

c. $\log \beta_n\{Cu(I) \text{ complex}\} - \log \beta_n \{Cu(II) \text{ complex})\}$.

It was assumed that the gold and platinum electrodes used in the present study would measure the potential changes of Au(I)/Au(0) and Cu(II)/Cu(I) couples E_{Au} and E_{Pt} respectively with time.

$$E_{Au} = E^o\{Au(I)/Au(0)\} + 0.059 \log \{\gamma_{Au(I)}\} + 0.059 \log\{[Au(I)]\} \quad (5.4)$$

$$E_{Pt} = E^o\{Cu(II)/Cu(I)\} + 0.059 \log \{\gamma_{Cu(II)}/\gamma_{Cu(I)}\} + 0.059 \log \{[Cu(II)]/Cu(I)]\} \quad (5.5)$$

However, in solutions which contained all four Au(c)/Au(I)/Cu(II)/Cu(I) species, both electrodes gave the same potential reading. As discussed in Chapter 4, this indicates that both electrodes measured the potential change of the Cu(II)/Cu(I) couple. In the absence of gold colloid, the measured potential of the platinum electrode should represent the copper(II)/copper(I) couple.

Most of the measurements were continued until the redox reaction equilibria were reached in both systems, at which point the values for E_{Pt}, and E_{Au} were recorded and the equilibrium concentrations [Cu(II)] or [Au(c)] were measured. These equilibrium potentials are compared with the calculated values at 25^{o}C based on the Nernst equation, assuming unit activity coefficients (γ).

The measured equilibrium potentials with reference to the standard hydrogen potential can be treated in two ways:

i) Direct comparison with the calculated potentials based on the Nernst equation (Eqs. 5.6 or 5.7), using appropriate values of E^{o} (Table 5.2), and concentrations of electro-active Au(I), or Cu(II)/(I) complex species.

ii) Conversion to E^{o} (Eqs. 5.8 and 5.9) and comparison with the E^{o} values based on the reported stability constants listed in Table 5.2.

$$E\{Cu(II)/Cu(I)\}_{cal.}$$

$$= E^{o}\{Cu(II)/(I)\} + 0.059 \log\{([Cu(II)][S_2O_3^{2-}]^{m})/([Cu(I)][NH_3]^{n})\} \quad (5.6)$$

$$E\{Au(I)/Au(0)\}_{cal}$$

$$= E^{o}\{Au(I)/(0)\} - 0.059 \log\{[S_2O_3^{2-}]^{2}/[Au(I)]\} \quad (5.7)$$

$E^o\{Cu(NH_3)_n^{2+}/Cu(S_2O_3)_m^{1-2m}\}_{cal}$

$= E_{meas.} - 0.059 \log \{([Cu(II)][S_2O_3^{2-}]^m)/ ([Cu(I)][NH_3]^n)\}$ (5.8)

$E^o\{AuL_2/Au(0)\}_{cal}$

$= E\{Au(I)/Au(0)\}_{(meas.)} - 0.059 \log [Au(I)] + 0.118 \log [L]$ (5.9)

The first method will reveal whether the measured potential reflects the calculated equilibrium value, which is based on the Nernst equation. Both methods will give information on actual electro-active metal ion complex species in the solutions.

5.3 Platinum electrode potentials during reaction

Figure 5.2 shows the measured platinum electrode potentials converted to $E_H = E_{meas} + E_{ref}$ for the lixiviant system, which contained copper(II), thiosulfate, and ammonia. The measured potential(s) attained constant values after 60 minutes, indicating that equilibria were reached. Fig. 5.3 shows a comparison between the changes in the platinum potentials with time, for the Cu(II)-NH_3-$S_2O_3^{2-}$ systems with nitrogen and with oxygen. In both cases the measured potentials reached equilibrium values after 5 hours, but the presence of oxygen resulted in higher potentials than were observed in reactions performed under nitrogen (Fig. 5.3). The measured equilibrium potentials are close to the calculated potentials of the couple(s) $Cu(NH_3)_3^{2+}/Cu(S_2O_3)_2^{3-}$ or $Cu(NH_3)_3^{2+}/Cu(S_2O_3)_3^{5-}$ (Fig. 5.2). However, in some cases, the potentials did not reach equilibrium values even after 6 hours (Fig. 5.4), depending on the conditions used.

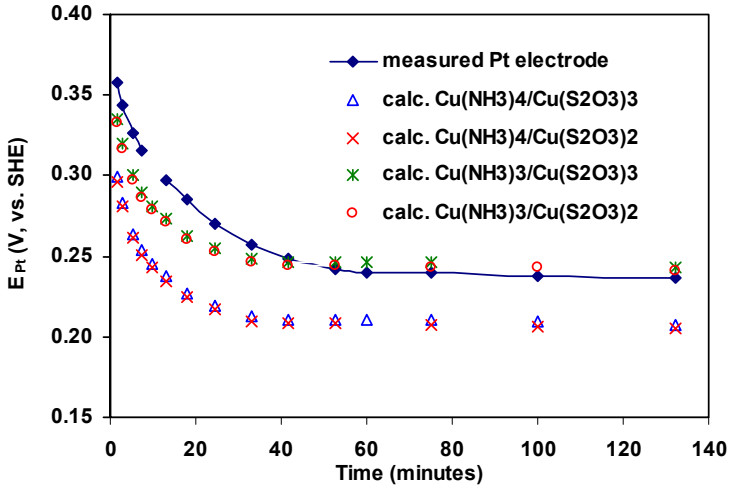


Fig. 5.2 *Measured and calculated potentials of platinum electrode in copper(II)-ammonia-thiosulfate solution under nitrogen atmosphere.*
40 mM $S_2O_3^{2-}$, 240 mM NH_3+NH_4^+, 2.0 mM Cu(II) and pH = 8.9.

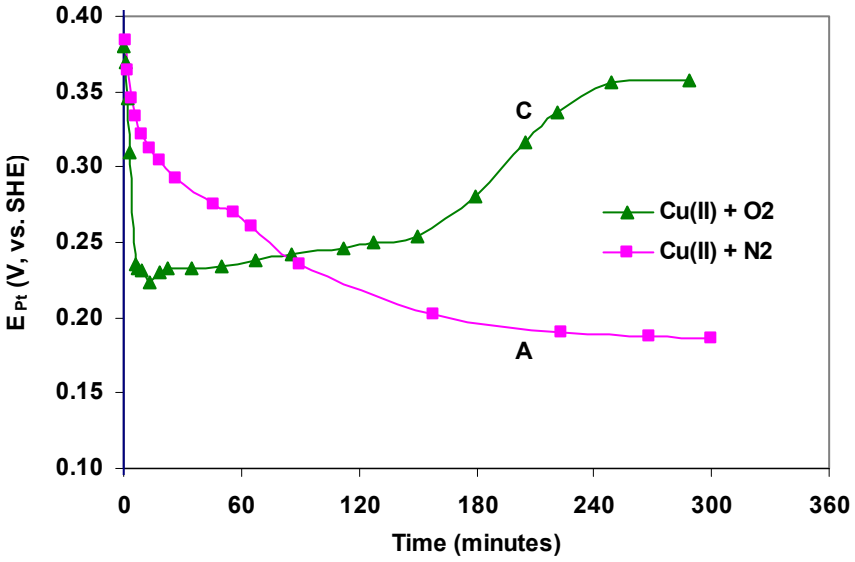


Fig. 5.3 *Measured potentials of platinum electrode in copper(II)-ammonia-thiosulfate solutions under nitrogen or oxygen atmosphere.*
50 mM $S_2O_3^{2-}$, 240 mM NH_3+NH_4^+, 2.0 mM Cu(II) and pH = 9.3.

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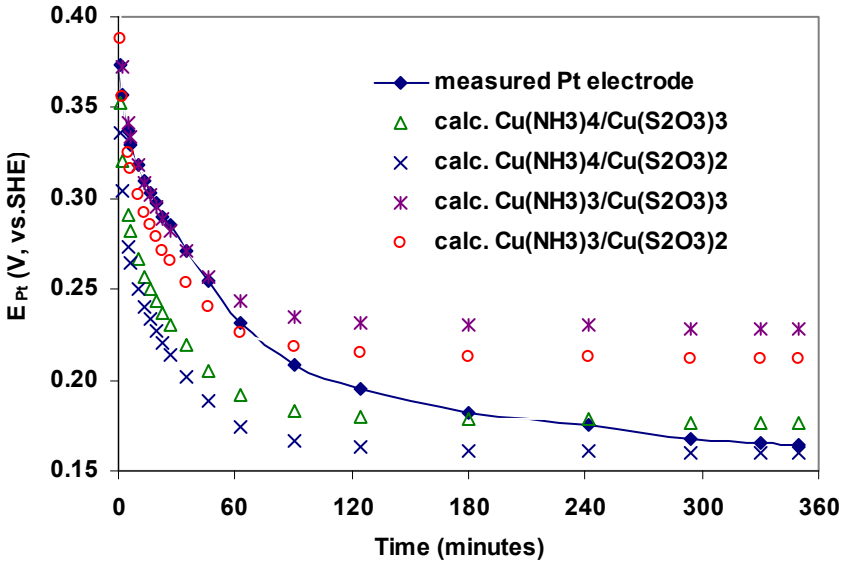


Fig. 5.4 *Measured and calculated potentials of platinum in copper(II)-ammonia-thiosulfate solution under nitrogen atmosphere.*
70 mM $S_2O_3^{2-}$, 240 mM NH_3+NH_4^+, 1.5 mM Cu(II) and pH = 9.3.

Table 5.3 compares the E^o{Cu(II)/Cu(I)} values based on the measured equilibrium potentials shown in Figs. 5.2 and 5.3. In some cases the measured values show reasonable agreement with the E^o{Cu(II)/Cu(I)} values calculated using stability constants. For example, the difference between the values of E^o based on measured equilibrium potentials and those predicted from stability constants for the two couples $Cu(NH_3)_3^{2+}$ /$Cu(S_2O_3)_3^{5-}$ and $Cu(NH_3)_3^{2+}$/$Cu(S_2O_3)_2^{3-}$ are less than 10 mV for Set A, in solutions of low thiosulfate and ammonia concentrations (A3S3 and A3S2 in Table 5.3). In the case of Set D, at higher ammonia and thiosulfate concentrations, the difference is smaller for the couple $Cu(NH_3)_4^{2+}$/$Cu(S_2O_3)_2^{3-}$. Thus, Table 5.3 shows that the coordination number of copper(II) can be 3 or 4 with respect to ammonia, while that of copper(I) can be 2 or 3 with respect to thiosulfate. This comparison does

not consider the mixed ammonia-thiosulfate complexes of copper(II) and copper(I) because of the lack of thermodynamic data for such complexes.

Table 5.3 *Comparison between measured and predicted $E^o\{Cu(NH_3)_n^{2+}/Cu(S_2O_3)_m^{1-2m}\}$ for different redox couples (n = 3 or 4, m = 2 or 3)*

Set	$[Na_2S_2O_3]$	$[NH_3]$	$[Cu(II)]_i$	[Cu(II)]/[Cu(I)]eq[a]		E^o{Cu(II)/Cu(I)}[b] for different couples[a] (V)[c]			
	mM	mM	mM	Ratio	E(V)	A4/S3	A4/S2	A3/S3	A3/S2
$[O_2]$ = 0 mM (under nitrogen)									
A	40(pH 8.9)	65	2.0	0.070	0.237	0.272	0.190	0.342	0.260
						(0.029)	(0.032)	(-0.007)	(-0.004)
B	50	120	1.5	0.074	0.194	0.273	0.197	0.328	0.251
						(0.030)	(0.039)	(-0.021)	(-0.013)
C	70	120	1.5	0.045	0.164	0.231	0.162	0.285	0.217
						(-0.012)	(0.004)	(-0.064)	(-0.047)
D	95	120	1.5	0.033	0.166	0.217	0.157	0.272	0.211
						(-0.026)	(-0.001)	(-0.077)	(-0.053)
$[O_2]$ = 0.31 mM									
E	20	120	2.0	7.1	0.355				
F	30	120	2.0	4.6	0.352				
G	50	144	3.0	2.9	0.352				

At 25°C, pH 9.3 and different initial ammonia and thiosulfate concentrations.

a. Based on measured copper(II) concentration using UV-VIS spectroscopy.

b. Values in parentheses show the difference E^o(meas) – E^o(calc).

c. A4 = $Cu(NH_3)_4^{2+}$, A3 = $Cu(NH_3)_3^{2+}$, A2 = $Cu(NH_3)_2^{2+}$, S3 = $Cu(S_2O_3)_3^{5-}$, S2 = $Cu(S_2O_3)_2^{3-}$.

It is also clear that in the absence of oxygen (Set A), the [Cu(II)]/[Cu(I)] ratios are two orders of magnitude lower than in the presence of oxygen (Set E). For example, an increase in [Cu(II)]/[Cu(I)] ratio from 0.033 (Set D) to 7.1 (Set E) should correspond to an increase in potential by 0.137 V, according to the Nernst equation: $E = E^{o} + 0.059\log\{Cu(II)/Cu(I)\}$. The actual increase in the measured potential was 0.189 V (from 0.166 V to 0.355 V), which was higher than the predicted 0.137 V. This reflects the difficulties in analysing the measured potentials in the presence of oxygen in sets E-G, due to:

(i) the rapid oxidation of thiosulfate species by copper(II) and/or oxygen during gold dissolution,

(ii) the involvement of other copper(II)/(I) complex species.

For example, Zhang and Nicol (2005) have proposed the formation of $Cu(S_2O_3)_3^{5-}.O_2$ based on electrochemical studies.

5.4 Gold electrode potentials

5.4.1 Effect of oxygen and copper(II)

Figure 5.5 shows the variation in the potential of a gold electrode immersed in oxygenated solutions that contained gold colloid and Au(I), where Au(I) was produced as a result of dissolution. For thiosulfate solution in the absence of ammonia, the measured potentials (line A, Fig. 5.5) reached a plateau after 2.5 hours of dissolution. The plateau potentials agree well with values calculated using the Nernst equation (Eq. 5.10), and the recently reported value of $E^o\{Au(S_2O_3)_2^{3-}/Au(0)\} = 0.274$ V (Senanayake et al., 2003).

$$E\{Au(I)/Au(0)\} = E^o\{Au(S_2O_3)_2^{3-}/Au(0)\} - 0.059 \log\{[S_2O_3^{2-}]^2/[Au(S_2O_3)_2^{3-}]\} \quad (5.10)$$

Likewise, the measured gold electrode potentials, in oxygenated ammoniacal thiosulfate solutions, agree with the calculated potentials (line B, Fig. 5.5). This indicates that the gold(I) species, produced in oxygenated thiosulfate solutions, is predominantly $Au(S_2O_3)_2^{3-}$. As shown in Fig. 5.6, there is close agreement between the measured and calculated gold potentials during the dissolution of gold colloid in copper(II)-ammonia-thiosulfate system. The measured values of E_{Au} in the oxygenated ammoniacal copper(II) thiosulfate solutions were generally higher than those calculated by substituting the gold(I) concentrations into Nernst equation (Fig. 5.7). However, the measured variation of E_{Au} in Fig.

5.7 (curve C) closely resembles that of E_{Pt} , representing the copper(II)/(I) couple in Fig. 5.3.

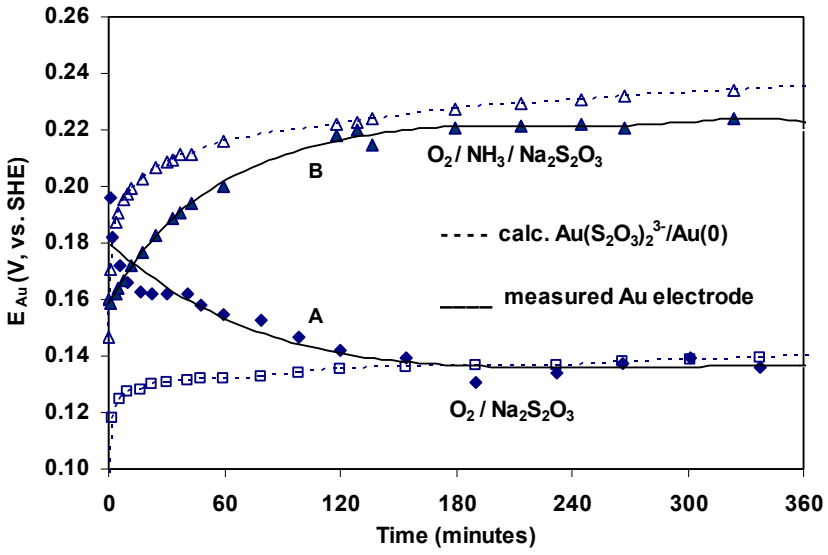


Fig. 5.5 *Measured and calculated potentials of gold electrode in oxygenated ammonia-thiosulfate solutions.120 mM NH_3, 0.25 mM O_2, pH 9.5 at 25°C, (A) 50 mM $Na_2S_2O_3$ and (B) 10 mM $Na_2S_2O_3$.*

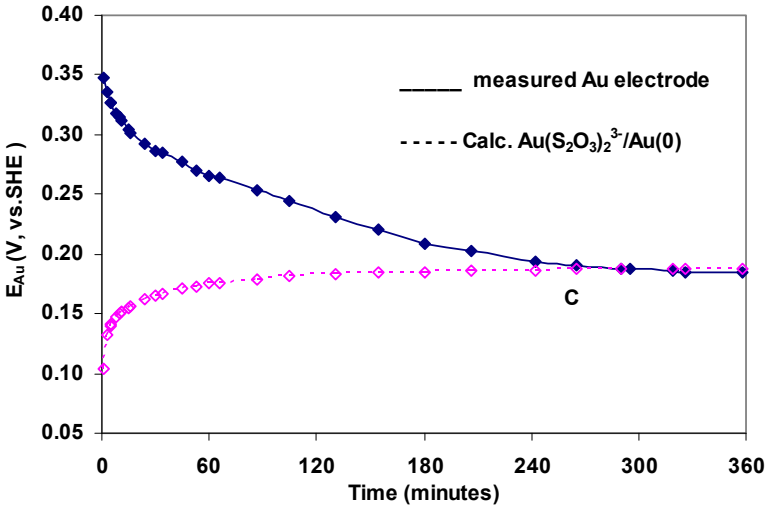


Fig. 5.6 *Measured and calculated potentials of gold electrode in copper(II)-ammonia-thiosulfate solutions under nitrogen.*
1.5 mM Cu(II), 50 mM $Na_2S_2O_3$, 240 mM NH_3+NH_4^+ and pH = 9.3.

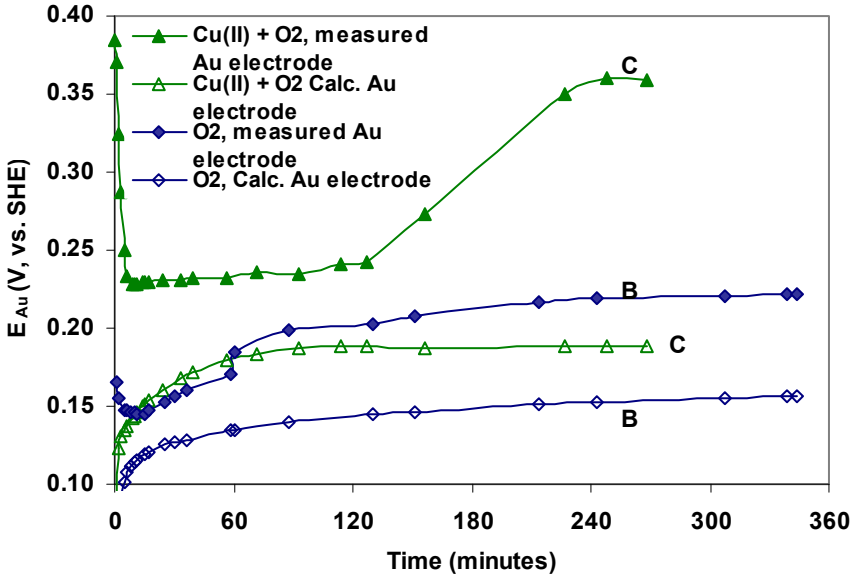


Fig. 5.7 *Comparison between measured and calculated potentials of gold electrode during gold dissolution*
Conditions: 50 mM $Na_2S_2O_3$, 240 mM NH_3+NH_4^+ at pH = 9.3.
B: 0.25 mM O_2,
C: 0.31 mM O_2 + 2.0 mM Cu(II).

5.4.2 Effect of ligand concentrations

(a) Ammoniacal-thiosulfate solution

The measured equilibrium potentials at 25°C can be used to calculate the values of E^o{Au(I)/Au(0)} according to Eq. 5.11 for the two ligands (L = $S_2O_3^{2-}$ or NH_3). This procedure is especially useful for the investigation of gold(I) species in oxygenated ammonia solutions in the absence of thiosulfate.

$$E^o\{Au(I)L_2/Au(0)\}$$
$$= E\{Au(I)/Au(0)\}_{(meas.)} - 0.059 \log[Au(I)] + 0.118 \log [L] \qquad (5.11)$$

Table 5.4 lists the measured potentials (corrected to SHE) as a function of concentrations of gold(I), thiosulfate, and ammonia. The calculated $E^o\{AuL_2/Au(0)\}$ values based on Eq. 5.11 are also included. The general trend is that $E^o\{AuL_2/Au(0)\}$ values increase with increasing concentrations of thiosulfate. However, it is of interest to note that the average of the first three values (0.275 ± 0.015 V) in the absence of ammonia is in close agreement with the value (0.274 V) reported recently, based on the linear free energy correlations (Senanayake et al., 2003).

(b) Thiosulfate-free ammonia solution

The oxygenated Cu(II)-NH_3 system without thiosulfate has been reported to be an effective lixiviant for gold at elevated temperatures and pressures (Han, 2001). At ambient temperatures and in the absence of thiosulfate, gold(I) produced from gold dissolution in the O_2-NH_3 system was either disproportionated or oxidized to a more stable $Au(NH_3)_4^{3+}$ complex according to Eqs. 5.12 and 5.13. Therefore, it is useful to compare the measured potentials with those calculated from the $Au(NH_3)_2^+/Au(0)$ or $Au(NH_3)_4^{3+}/Au(0)$ couple, as shown in Eqs. 5.14 and 5.15.

$$3Au(NH_3)_2^+ = 2Au(c \text{ or } s) + Au(NH_3)_4^{3+} + 2NH_3 \quad (5.12)$$

$$2Au(NH_3)_2^+ + O_2 + 4NH_4^+ = 2Au(NH_3)_4^{3+} + 2H_2O \quad (5.13)$$

$$E^o\{Au(NH_3)_2^+/Au(0)\}$$

$$= E\{Au(I)/Au(0)_{(meas.)}\} - 0.059 \log [Au(I)] + 0.118 \log [NH_3] \quad (5.14)$$

$E^o\{Au(NH_3)_4^{3+}/Au(0)\}$

$= E\{Au(III)/Au(0)_{(meas.)}\} - (0.059/3) \log [Au(III)] + (0.236/3) \log [NH_3]$ (5.15)

Table 5.4. *Effect of initial reagent concentration on measured equilibrium potential (E, SHE) and E^o for gold(I)/(0) redox couple*

Set	$[Na_2S_2O_3]$ mM	$[NH_3]$ mM	$[O_2]$ mM	$[Cu(II)]_i$ mM	$[Au(c)]_{eq}$ 10^{-5} M	$[Au(I)]_{eq}$ 10^{-5} M	Au(I)/Au(0) potential E(V)	E^o(V)
A	30	0	0.25	0	8.86	1.14	0.150	0.262
A	50	0	0.25	0	8.78	1.22	0.138	0.274
A	70	0	0.25	0	8.67	1.33	0.139	0.290
A	10	120	0.25	0	7.70	2.30	0.219	0.257
A	20	120	0.25	0	8.00	2.00	0.226	0.303
B	10	240	0	1.5	0.63	9.37	0.226	0.228
B	20	240	0	1.5	0.28	9.72	0.220	0.256
B	30	240	0	1.5	0.76	9.24	0.215	0.273
B	50	240	0	1.5	1.10	8.90	0.185	0.270
B	70	240	0	1.5	1.65	8.35	0.178	0.282
B	95	240	0	1.5	3.94	6.06	0.141	0.269

pH 9.5 (set A), pH 9.3 (set B) at 25°C; E^o calculated using Eq. 5.9.

Figure 5.8 compare the measured and calculated gold potentials in ammoniacal solutions in the presence of copper(II) or oxygen as the oxidant, but without thiosulfate. Agreement between the measured and the calculated values has not been observed in either case.

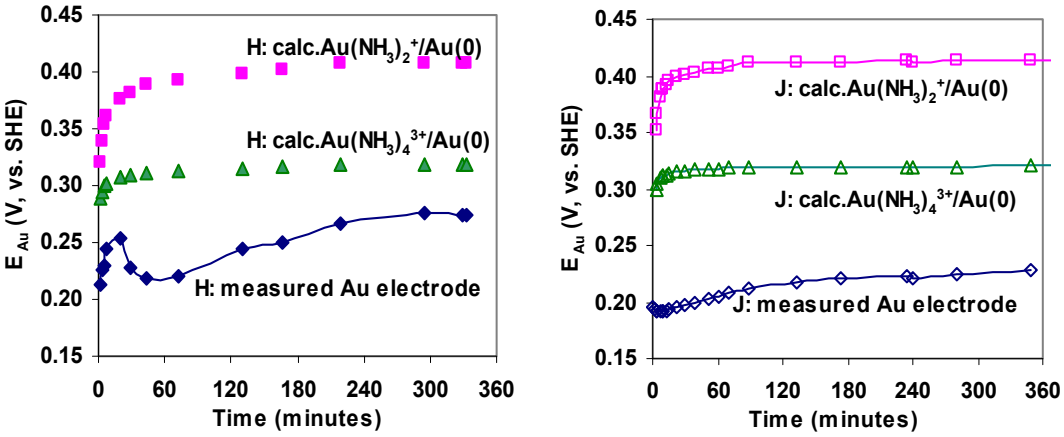


Fig. 5.8 *Measured and calculated potentials of gold electrode in ammonia solutions without thiosulfate*
0 mM $Na_2S_2O_3$, 120 mM NH_3+NH_4^+ at pH 9.5,
H: 2.5 mM Cu(II), J: 0.25 mM [O_2].

The results presented in Table 5.5 show that the measured potential of a gold electrode decreases with increasing ammonia concentrations. Unlike the cases shown in Table 5.4, the calculated values of $E^o\{Au(NH_3)_2^+/Au(0)\}$ and $E^o\{Au(NH_3)_4^{3+}/Au(0)\}$ differ significantly from the reported values of 0.563 V and 0.325 V respectively (Skibsted and Bjerrum, 1974). The measured gold electrode potentials in the range 0.205 V to 0.245 V (Table 5.5) in the oxygenated ammonia solutions are consistent with the value of $E^o\{Au(NH_3)_4^{3+}/Au(NH_3)_2^+\}$ = 0.206 V reported by Skibsted and Bjerrum (1974). However, a detailed analysis of these results is beyond the scope of the present investigation, because data on the individual concentrations of Au(I) and Au(III) are not available.

Table 5.5 *Effect of initial reagent concentrations on measured equilibrium potential (E, SHE) and E^o for gold(I)/(0) redox couple*

Set	$[NH_3]$ mM	$[O_2]$ mM	$[Cu(II)]_i$ mM	$[Au(c)]_{eq}$ 10^{-5} M	[Au(I) or (III)]$_{eq}$ 10^{-5} M	E_{Au} meas.V	E^o{Au(I or III)/Au(0)}$_{calc.}$ V	
							$E^oAu(I)/(0)$	$E^oAu(III)/(0)$
A	40	0.25	0	8.83	1.17	0.245	0.374	0.234
A	70	0.25	0	8.89	1.11	0.234	0.392	0.242
A	130	0.25	0	8.67	1.33	0.210	0.404	0.235
A	170	0.25	0	8.72	1.28	0.205	0.364	0.242
B	72	0	2.5	9.6	0.4	0.275	0.431	0.282
B	36	0	1.5	9.8	0.2	0.274	0.440	0.273
B	108	0	1.5	9.8	0.2	0.249	0.471	0.285
B	144	0	1.5	9.7	0.3	0.258	0.485	0.300

at 25^{o}C, pH 9.5 in thiosulfate free solutions.

5.4.3 Effect of background salts

Figures 5.9 - 5.11 compare the measured and calculated gold electrode potentials, during gold dissolution in the presence of background salts such as NaCl, $AgNO_3$, Na_2CO_3, $Na_2S_3O_6$ and Na_2SO_3. In the cases of NaCl, $AgNO_3$, Na_2CO_3 and $Na_2S_3O_6$, there is close agreement between the measured and calculated potentials at equilibrium (Figs. 5.9 - 5.11). However, the presence of Na_2SO_3 lowers the measured gold potentials (Fig. 5.11). This may be attributed to the formation of a gold(I) complex involving sulfite as a ligand $Au(S_2O_3)(SO_3)^{3-}$ (Perera et al., 2005).

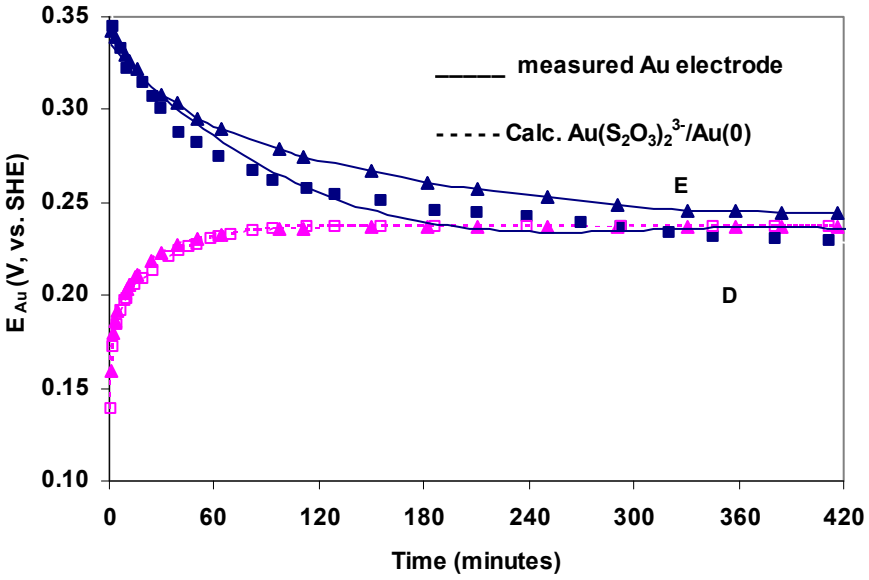


Fig. 5.9 *Measured and calculated potentials of gold electrode in copper(II)-ammonia-thiosulfate-silver(I) or chloride solution.*
1.5 mM Cu(II), 20 mM $Na_2S_2O_3$,120 mM NH_3+NH_4^+ , and pH 9.5.
D: 330 mM NaCl and E: 0.1 mM $AgNO_3$.

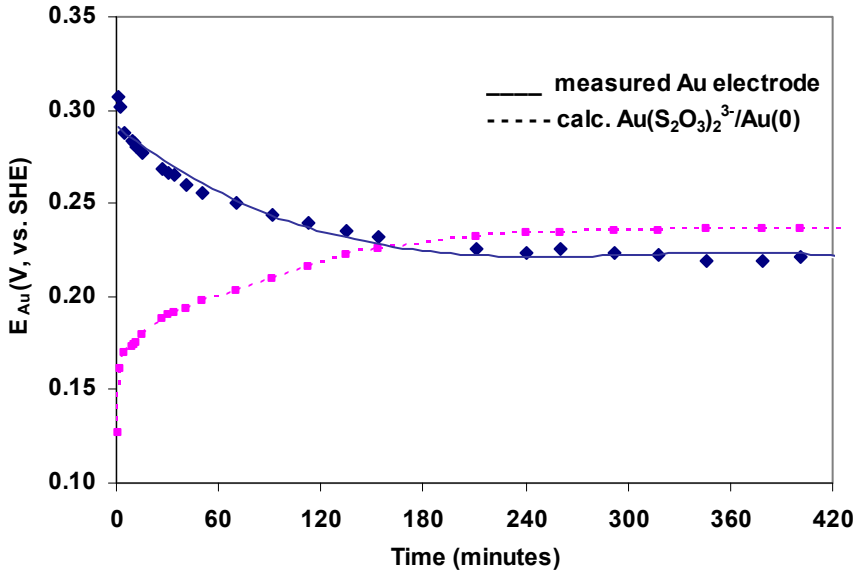


Fig. 5.10 *Measured and calculated potentials of gold electrode in copper(II)-ammonia-thiosulfate-carbonate solution.*
1.5 mM Cu(II), 20 mM $Na_2S_2O_3$, 120 mM NH_3+NH_4^+, 110 mM Na_2CO_3, pH 9.5.

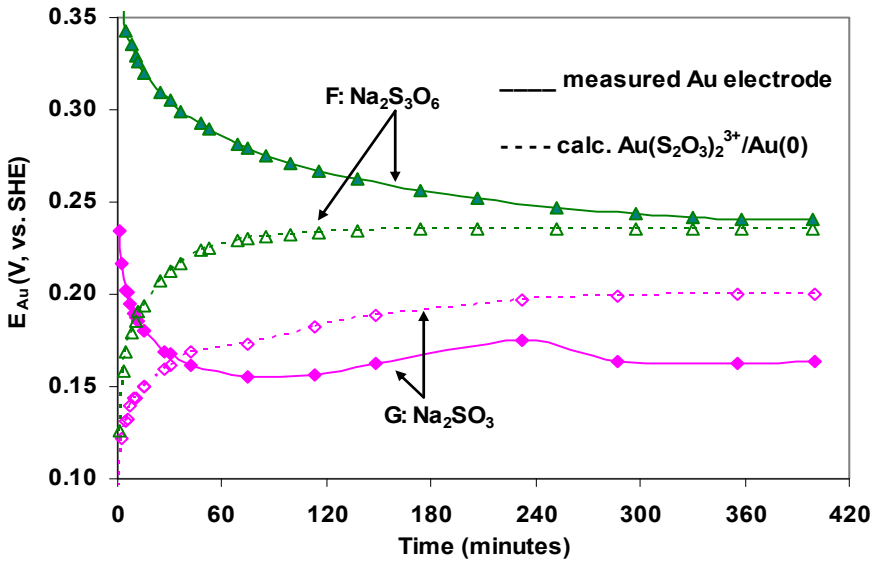


Fig. 5.11 *Measured and calculated potentials of gold electrode in copper(II)-ammonia-thiosulfate-sulfite or trithionate solutions.*
1.5 mM Cu(II), 20 mM $Na_2S_2O_3$, 120 mM NH_3+NH_4^+, pH 9.5.
F: 20 mM $Na_2S_3O_6$, G: 40 mM Na_2SO_3.

5.5 Summary and conclusions

The complex $Au(S_2O_3)_2^{3-}$ has been identified as the predominant gold(I) species in lixiviant solutions containing ammonia and thiosulfate, and is produced by the oxidation of gold by oxygen or copper(II). In the absence of thiosulfate, the measured gold potentials were in close agreement with those reported for the $Au(NH_3)_4^{3+}/Au(NH_3)_2^+$ couple, indicating that disproportionation or oxidation of $Au(NH_3)_2^+$ occurs during dissolution. In the copper-ammonia-thiosulfate system, the results suggest that the platinum electrode measures the potential of the $Cu(NH_3)_n^{2+}/Cu(S_2O_3)_m^{(1-2m)+}$ couple, with n = 4 or 3, m = 3 or 2, depending on the reaction conditions. The presence of trithionate, carbonate or chloride ions showed no effect on the nature of the gold(I)/(0) couple. However, sulfite ions in

the solution may interact with gold(I) to form a complex, and may therefore lower the gold(I)/gold(0) potential.

CHAPTER 6 INITIAL RATES OF GOLD DISSOLUTION

6.1 Introduction

The rate of a chemical reaction is defined as the rate of change of concentration of reactants or products (Nicholas, 1976). In a kinetic study, the concentration of a reactant or a product is determined experimentally and plotted as a function of time. The slope of such curves represents the rate at any given time. In the case of gold dissolution in ammoniacal copper(II) thiosulfate solutions, the reaction between copper(II) and thiosulfate would change the concentration of reagents with time and affect the kinetics of gold dissolution. Thus, it is more appropriate to use the initial slope, at $t \rightarrow 0$, which gives the rate of the reaction corresponding to the initial concentrations of reagents. This method of determining the initial slope is known as the differential method (Laidler, 1965), and will be used in this thesis. Dealing with initial rates also avoids possible complications due to interference from by-products, such as sulfoxy anions produced as a result of the oxidation of thiosulfate, and leads to a reaction order which corresponds to the simplest type of situation. Reliable information on reaction order with respect to the concentration of different reagents is useful in the discussion of reaction mechanism.

Previous researchers have analysed the initial rates of gold dissolution from colloids and flat surfaces in cyanide or thiosulfate media on the basis of the Levich equation (Jeffrey, 2001) and shrinking sphere model (McCarthy et al. 1998). It is important to revise the relevant mathematical relationships and

compare and contrast the rate of dissolution of gold in thiosulfate and cyanide media to examine the validity of the kinetic treatment presented in this thesis.

In this chapter the curves for gold dissolution in different lixiviant systems are compared in order to examine the effect of single ligands (ammonia, thiosulfate, chloride) and mixed-ligands, as well as oxidants such as oxygen, copper(II), and copper(II)-oxygen as a mixed oxidant. The main topics covered are:

(i) comparison of gold dissolution in different lixiviant systems,

(ii) methods of quantitative analysis of gold dissolution to obtain initial rates,

(iii) determination of activation energies from initial rates of gold oxidation by oxygen or copper(II) to examine the chemically or diffusion controlled nature of the surface reaction,

(iv) comparison of the effect of change in concentration of each reagent on initial rate and the extent of gold dissolution,

(v) comparison of the effect of background salts on the initial rates of gold dissolution.

Literature data based on rotating discs are used to show that the Levich equation is applicable for the initial rate of dissolution of silver and gold-silver alloy of 5% silver from flat surfaces. The non applicability of the Levich equation for the dissolution of gold-silver alloy from flat surfaces in thiosulfate media at high concentrations of copper(II) is highlighted. The effect of background reagents on initial rates is used to propose a reaction scheme for gold dissolution in ammoniacal copper(II) thiosulfate solutions.

6.2 Gold dissolution in different lixiviant systems

Figure 6.1 shows the extent of gold dissolution as a function of time in different lixiviant systems. As can been seen, the O_2-CN^- system was the fastest, with over 95% of gold dissolved in 2 minutes (curve a). The Cu(II)-NH_3-N_2 system in the absence of thiosulfate was the slowest at 25^oC, although the rate (slope of curve) and extent of gold dissolution increased slightly at 48^oC (curves e and d). In the case of the Cu(II)-NH_3-$S_2O_3^{2-}$-N_2 system, the initial rate and the dissolution after 6 - 7 hours depended upon the concentration of reagents. For example, with 4.5 mM Cu(II), the dissolution was almost 90% in 1 hour and over 96% in 2 hours (curve b). These values decreased to 35% (1 hour) and 45% (2 hours) respectively when the Cu(II) concentration was reduced to 0.5 mM (curve c).

Figure 6.2 shows that the replacement of N_2 by air (curve g, reactor open to air) had only a slightly negative effect, while the use of 0.5 mM O_2 (sparging O_2, curve h) resulted in the dissolution ceasing at 60% in 1.5 hours. These findings indicate that excess O_2 has a detrimental effect on the kinetics of gold dissolution.

Figure 6.3 shows the results relevant to the dissolution of gold in oxygenated solutions in the absence of copper(II). In the O_2-NH_3 and O_2-$S_2O_3^{2-}$ systems, only about 10% of the gold was dissolved in 1.5 hours. The latter produced a faster initial rate (curve k versus curve m in Fig. 6.3), compared to 2% dissolved by Cu(II)-NH_3 at similar concentrations (curve e in Fig. 6.1). The presence of

both ligands (NH_3 and $S_2O_3^{2-}$) apparently increased the dissolution. Further improvement was obtained when the oxygen concentration was increased from 0.25 mM to 0.5 mM, where more than 35% gold was dissolved in 5 hours. However, this value was still significantly lower than that obtained in the 0.5 mM Cu(II)-N_2 system (curve c in Fig. 6.1), indicating that copper(II) is a more effective oxidant than oxygen for the leaching of gold in thiosulfate solutions. Figure 6.4 compares the effect of O_2, Cu(II) and Cu(II) + O_2 on gold dissolution. It is clear that copper(II) is a more efficient oxidant than oxygen alone. In the case of mixed oxidants (Cu(II) + O_2), although the presence of oxygen slows down the initial dissolution, it is beneficial in terms of the final extent of gold dissolution.

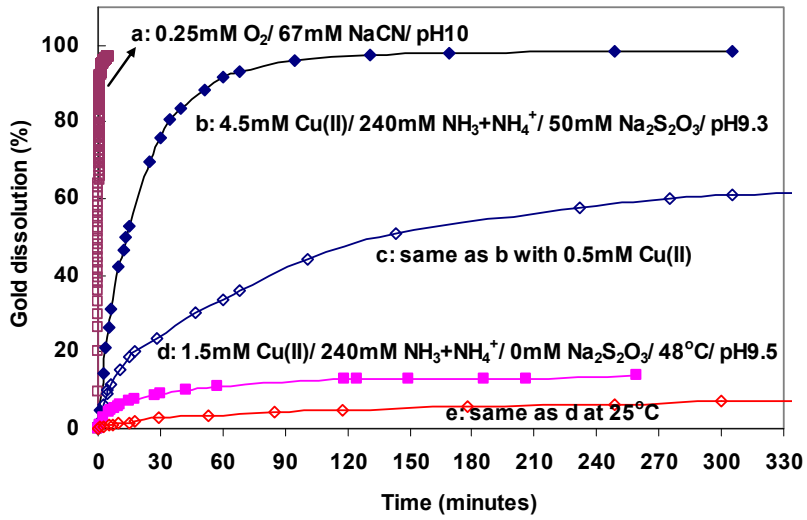


Fig. 6.1 *Dissolution of gold in different solution systems at 25°C.*

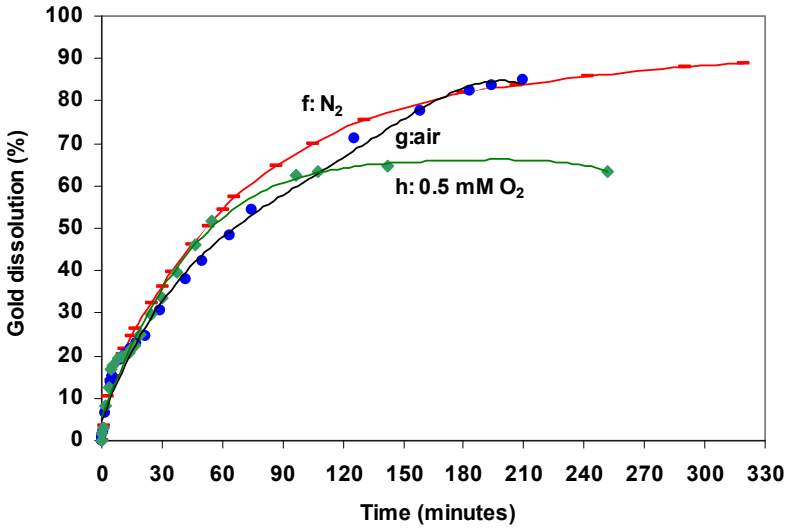


Fig. 6.2 *Effect of sparging nitrogen, air or oxygen on gold dissolution in copper(II)-ammonia-thiosulfate solutions.*
1.5 mM Cu(II), 240 mM NH_3+NH_4^+, 50 mM $Na_2S_2O_3$ at pH 9.5, 25 °C.

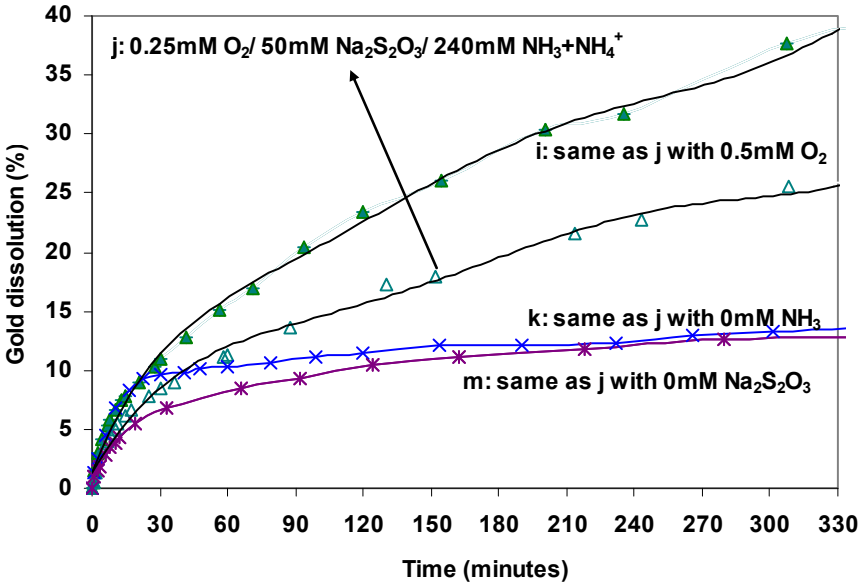


Fig. 6.3 *Effect of ammonia, thiosulfate, and dissolved oxygen on gold dissolution in non-copper(II) solutions.*
pH 9.5, 25 °C.

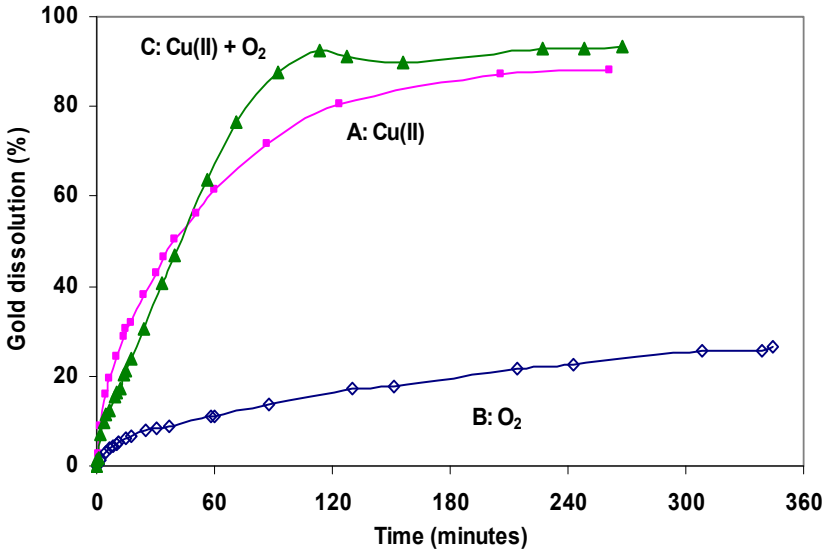


Fig. 6.4 *Effect of oxygen and/or copper(II) on gold dissolution in ammonia-thiosulfate solutions. 50 mM $Na_2S_2O_3$, 240 mM NH_3+NH_4^+, pH 9.3. A: 2.0 mM Cu(II), B: 0.25 mM O_2, C: 2.0 mM Cu(II) + 0.31 mM O_2.*

6.3 Oxidation of thiosulfate by oxygen or copper(II)

In the absence of copper(II), the oxidation of thiosulfate by oxygen at ambient conditions was found to be very slow, but increasing temperature and pressure dramatically increased the oxidation rate (Rolia and Chakrabarti, 1982; Ji et al., 2003; Jiang et al., 1996). In experiments conducted in this study using oxygen-thiosulfate-ammonia solution, there was no detectable decomposition of thiosulfate in the first hour and only 6% of thiosulfate decomposed in 5 hours (Table 6.1). Thus, the thiosulfate concentration remained approximately unchanged and sufficient for gold dissolution. This allows changes in initial reaction rate to be interpreted on the basis of other factors.

Table 6.1 *Decrease in thiosulfate concentration with time*

Time (min.)	0	60	120	180	245	300
$[S_2O_3^{2-}]$ (mM)	50	50	49.8	49	48.5	47.1
Decomposition %	0	0	0.4	2	3	6

$[O_2]$ = 0.75 mM, $[NH_3+NH_4^+]$ = 240 mM, pH = 9.3, 25^oC.

However, the reaction of Cu(II) with thiosulfate leads to the formation of tetrathionate, which undergoes conversion to trithionate and thiosulfate as described in Section 2.3.2 (Byerley et al., 1973b; Zhang and Dreisinger, 2002). Consequently, the formation of a series of stable and metastable sulfur-oxy species such as tetrathionate, pentathionate, trithionate, sulfite and sulfate increases thiosulfate consumption (Byerley et al., 1973a,b; 1975) and lowers the concentrations of thiosulfate and copper(II). Thus, the analysis of rate data for gold dissolution in an ammoniacal copper(II) thiosulfate solution is more complex than that of gold cyanidation, mainly due to the background reaction between copper(II) and thiosulfate.

For example, a log-log plot of gold dissolution rate (d[Au(I)]/dt) against thiosulfate oxidation rate ($-d[S_2O_3]/dt$) expressed in mol L^{-1} h^{-1} (Muir and Aylmore, 2004) shows a linear relationship with a slope close to 1 in ammoniacal thiosulfate solution (Eq. 6.1) (Senanayake, 2004a).

$$d[Au(I)]/dt = -d[S_2O_3^{2-}]/dt \quad -3.71 \qquad (R^2 = 0.98) \qquad (6.1)$$

Moreover, as shown in Fig. 6.5, not only is the dissolution of gold in the copper(II)-ammonia-thiosulfate media much slower than that in the cyanide

media, it is also quite sensitive to the initial concentration of gold. The presence of gelatine, adsorption or desorption of various ions in the initial solution or those formed during reaction, as well as the decrease in particle size and surface area, are likely to be responsible for the variation among the dissolution curves with variation in the initial concentration of gold and time.

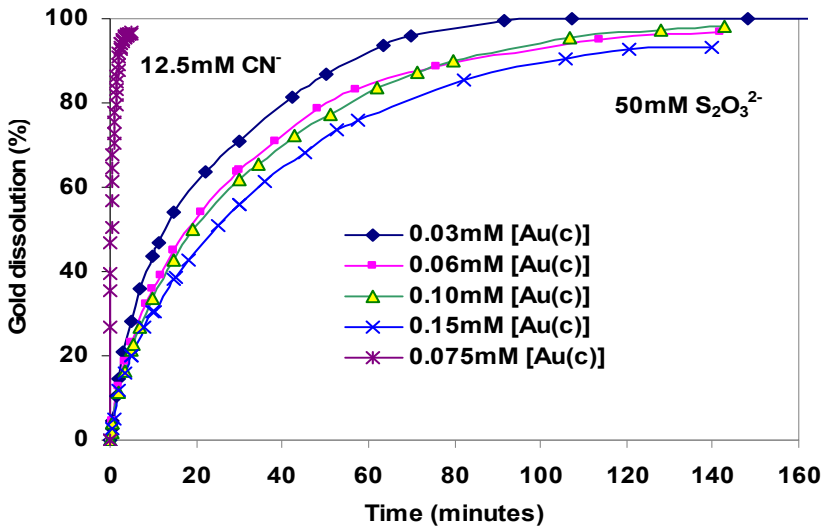


Fig. 6.5 *Comparison of gold dissolution in cyanide and thiosulfate solutions*
$[O_2]$ = 0.25mM, pH 10.1 (cyanide solution);
$[Cu(II)]$ = 2.0 mM, $[NH_3+NH_4^+]$ = 240 mM, pH 9.5 (thiosulfate solution).

The extent of oxidation of thiosulfate by copper(II) in ammoniacal solutions in the presence of oxygen is very high (Chu et al., 2003). The initial rate of thiosulfate consumption is 40 times higher than that in the absence of oxygen (Byerley et al., 1975). However, the oxidation of thiosulfate by copper(II) in the absence of oxygen is limited because copper(II) is not reproduced (Byerley, 1973b; Breuer and Jeffrey 2003b; Chu et al., 2003).

In the initial stages, copper(II) competes to react with gold and thiosulfate, where the latter produce polythionates such as tetrathionate and trithionate.

Breuer and Jeffrey (2002), Muir and Aylmore (2002), and Chu et al. (2003) reported that tetrathionate and trithionate had little effect on gold oxidation and leaching kinetics compared to the effect of disulfite. Recent studies by Feng and van Deventer (2007c) showed beneficial effects of sulfur species at low concentration levels. Thus, it is important to consider the initial rates of gold oxidation ($t \rightarrow 0$) so that the effect of temperature, pH, ionic strength and the initial concentration of reagents including polythionates can be analysed to rationalise the reaction mechanism, because the polythionates produced can be ignored at $t \rightarrow 0$.

6.4 Determination of initial rates

6.4.1 Thiosulfate media

The rate of a chemical reaction may be expressed as the rate of decrease of the concentration of a reactant. Thus, the rate of dissolution of gold in ammoniacal copper(II) thiosulfate according to Eq. 6.2 can be expressed by Eq. 6.3, where a, and b are the reaction orders with respect to gold and copper(II) respectively. Assuming a = 1 and integrating within the limits $[Au(c)]_{t=0}$ at time $\rightarrow 0$ and $[Au(c)]_t$ at time t, the rate equation can be simplified to Eq. 6.5. Therefore, at given concentrations of copper(II), a plot of $\ln\{[Au(c)]_{t=0}/[Au(c)]_t\}$ as a function of time can be used to examine the validity of Eq. 6.5. Since gold colloids obey the Beer Lamberts Law, the absorbance ratio $\ln\{A_o/A_t\}$ can be used instead of $\ln\{[Au(c)]_{t=0}/[Au(c)]_t\}$ (Eq. 6.6).

$$Au(c) + Cu(II) = Au(I) + Cu(I) \quad (6.2)$$

$$-d[Au(c)]/dt = k[Au(c)]^a[Cu(II)]^b \quad (6.3)$$

$$-\{d[Au(c)]\}/[Au(c)] = k[Cu(II)]^b\, dt \quad (a = 1) \quad (6.4)$$

$$\ln \{[Au(c)]_{t=0}/[Au(c)]_t\} = k[Cu(II)]^b\, t = k_1\, t \quad (6.5)$$

$$\ln \{A_0/A_t\} = k[Cu(II)]^b\, t = k_1\, t \quad (6.6)$$

$$\ln k_1 = \ln k + b \ln[Cu(II)] \quad (6.7)$$

Figure 6.6a shows a plot of ln (A_o/A_t) as a function of t, to examine the effect of gold colloid concentration on dissolution kinetics. A linear relationship with $R^2 > 0.99$ is shown only in the case of 0.1 mM gold colloid, confirming the validity of Eq. 6.6 and a first order reaction (a = 1). Since the concentrations of reagents change with time due to side reactions, it is more appropriate to examine the rate curve in the initial 10 minutes or 15 minutes. Fig. 6.6b shows a good binomial fit (Eqs. 6.8 - 6.9) to the gold dissolution curve over the first 10 minutes.

$$[Au(c)]_t = a\, t^2 + b\, t + c \quad (6.8)$$

$$[Au(c)]_t = 0.0002\, t^2 - 0.0036\, t + 0.0996 \quad (6.9)$$

$$-d[Au(c)]/dt = -2\, a\, t - b \quad (6.10)$$

$$R_i = -d[Au(c)]/dt = -b \text{ (initial rate at } t = 0) \quad (6.11)$$

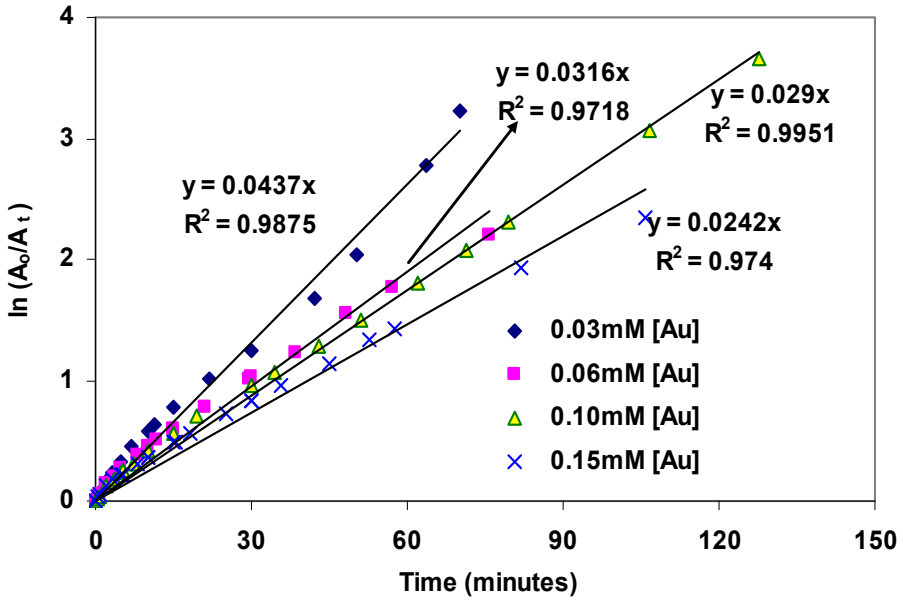


Fig. 6.6a *A plot of ln(A_o/A_t) versus time in gold-copper(II)-ammonia-thiosulfate solution.*

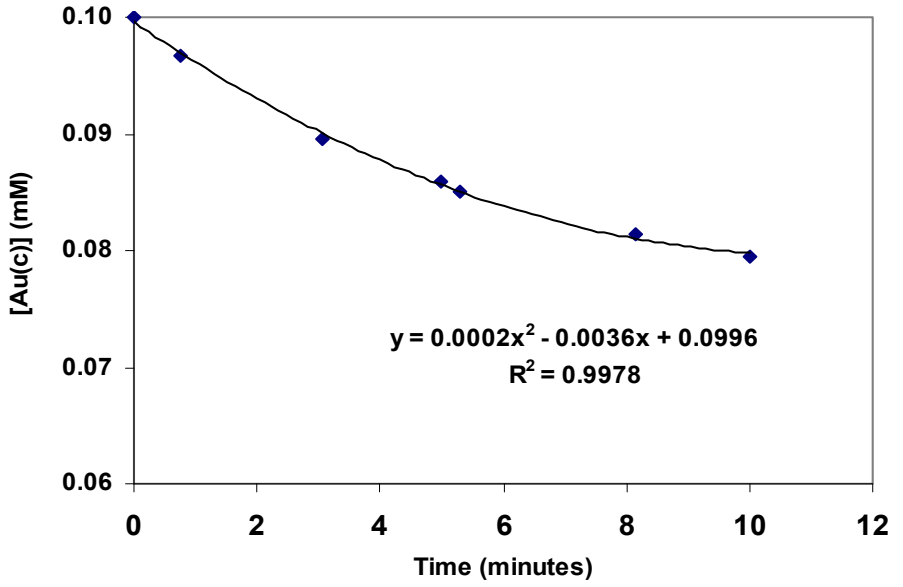


Fig. 6.6b *Initial gold dissolution in copper(II)-ammomina-thiosulfate solution. [Cu(II)] = 2.0 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.*

Thus, Eq. 6.11 can be used to determine the initial rate (R_i) of gold dissolution as a function of the concentration of gold colloid, based on the curves in Fig. 6.5. Table 6.2 gives the values of R_i (μM/min or mol L^{-1} s^{-1}). Likewise, Table 6.3 lists the two sets of values of R_i (mol L^{-1} s^{-1}) to show the effect of particle size in the cases of powder, stabilized, and unstabilized colloids. The slope of the logarithmic plot of R_i as a function of particle size of stabilized colloids is -1, as shown in Fig. 6.7.

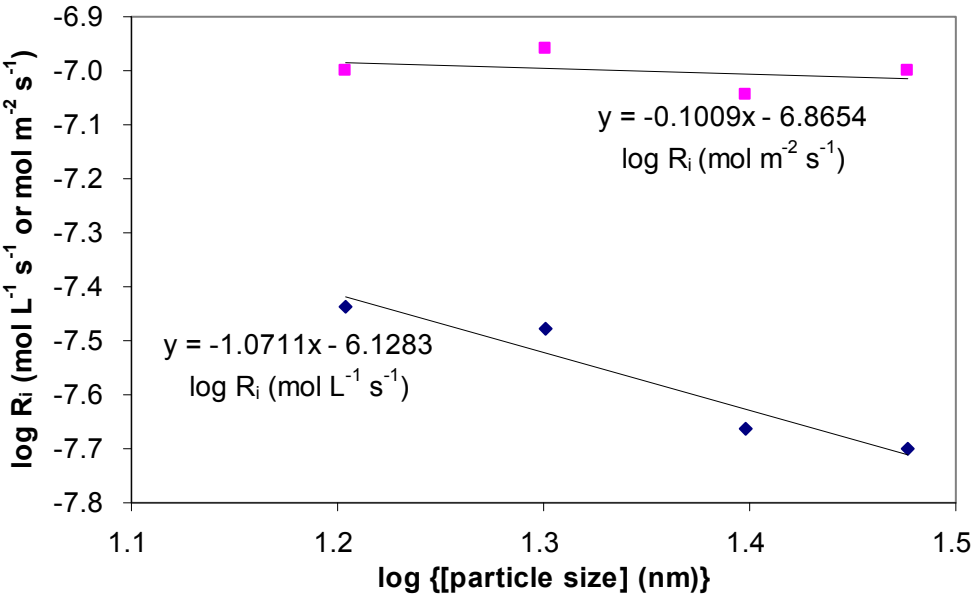


Fig. 6.7 *Logarithmic plot of initial rates (R_i) as a function of particle size of stabilized colloids in copper(II)-ammonia-thiosulfate solutions.*

The initial rates of dissolution R_i (μM min^{-1}) or R_i (mol L^{-1} s^{-1}) can also be expressed in the form of R_i (mol m^{-2} s^{-1}), which allows the comparison between the rate of dissolution per unit area of gold colloids with massive gold based on rotating disc studies reported by Jeffrey (2001). The following equations were used to convert R_i (mol $L^{-1}s^{-1}$) to R_i (mol m^{-2} s^{-1}):

$S = 4\pi r^2$ = surface area of a colloid particle (m^2 $particle^{-1}$)

$V = (4/3)\pi r^3$ = volume of a colloid particle (m^3 $particle^{-1}$)

r = radius of gold colloid particle (m)

W = d*V = mass of a colloid particle (g $particle^{-1}$)

d = mass of unit volume of gold colloid or pure gold (g m^{-3}) = density

$S_T = n * S$ = total surface area of one mole of gold colloid or powder (m^2 mol^{-1})

n = 197/W = number of colloid particles in 1 mol (particles mol^{-1})

R_i (mol m^{-2} s^{-1}) = {R_i (mol $L^{-1}s^{-1}$)}/{S_T (m^2 mol^{-1}) * C (mol L^{-1})}

C = concentration of gold in colloidal dispersion (mol L^{-1})

Tables 6.2 and 6.3 list the values of R_i (mol m^{-2} s^{-1}) and show that the rate per unit area (R_i mol m^{-2} s^{-1}) of different types of gold is relatively unaffected compared to the values expressed as R_i (μm min^{-1}). It can be seen that the increase in rate with increasing concentration and/or decrease in particle size is a result of the increasing surface area. Gold powder and unstabilized gold colloids have a higher rate of dissolution compared to gelatine stabilized colloids. This may be related to a high surface roughness factor in the case of gold powder, and without gelatine coating in the case of unstabilized colloids. Moreover, the results from this study for the dissolution of gold colloids in cyanide and thiosulfate media can be compared with the literature data (Jeffrey and Ritchie, 2001; Jeffrey, 2001) on the basis of R_i (mol m^{-2} s^{-1}), to examine the validity of the kinetic treatment.

Table 6.2 *Effect of gold concentration on initial rate (R_i)*

[Au(c)] (mM)	0.03	0.06	0.1	0.15
R_i (μM min^{-1})	1.9	3.4	5.1	7.3
10^8 R_i (mol L^{-1} s^{-1})	3.2	5.7	8.5	12
10^6 R_i (mol m^{-2} s^{-1})	0.35	0.32	0.28	0.27

[Cu(II)] = 2.0 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.

Table 6.3 *Effect of particle size of gold on initial rate (R_i)*

Particle type	Gelatine stabilized				Unstabilized		Powder	
Size (nm)	16	20	25	30	10	32	2250	7250
R_i (μM min^{-1})	2.2	2.0	1.3	1.2	16.4	2.5	0.075	0.046
10^8 R_i (mol L^{-1} s^{-1})	3.7	3.3	2.2	2.0	27.3	4.2	0.13	0.077
10^6 R_i (mol m^{-2} s^{-1})	0.10	0.11	0.09	0.10	0.47	0.22	0.47	0.93

[Cu(II)] = 2.0 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.

6.4.2 Cyanide media

A comparison of the effect of cyanide concentration, pH, and ionic strength on R_i (mol L^{-1} s^{-1}) and R_i (mol m^{-2} s^{-1}) based on the results obtained in the present study is made in Table 6.4. Fig. 6.8 plots log R_i as a function of log [CN^-] and compares the literature data for massive gold reported by Jeffery and Ritchie (2001) based on rotating electrode quartz crystal microbalance. The agreement between stabilized colloidal gold and massive gold is within an order of magnitude, while the higher rates in lines A and B can be related to low pH of 10.

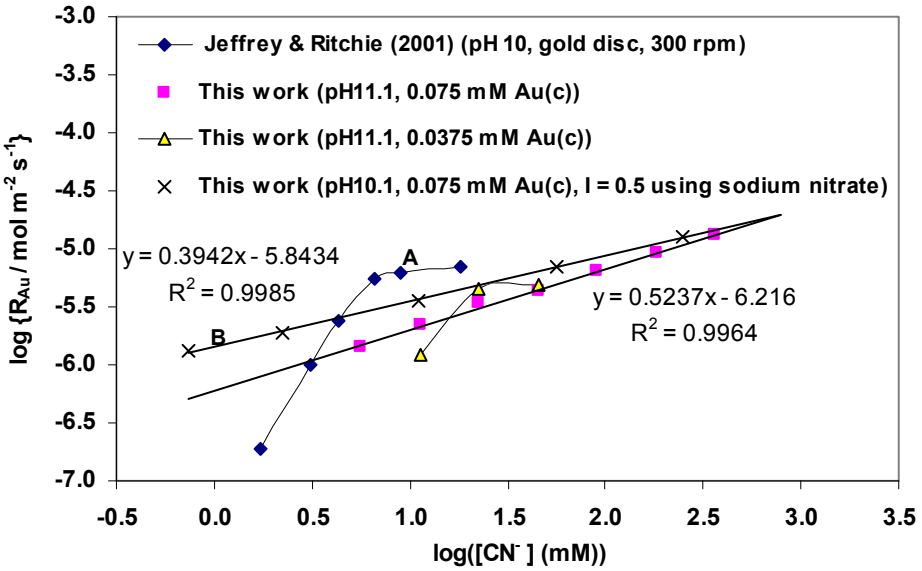


Fig. 6.8 *Effect of cyanide concentration on rates of cyanidation of colloidal gold and massive impurity-free gold at 25°C.*
(Data from Table 6.4 and Jeffrey and Ritchie, 2001).

Table 6.4 *Initial rates for cyanidation*

$[CN^-]$ (mM)	[Au(c)] (mM)	I	pH	R_i mol $L^{-1}s^{-1}$	R_i mol $m^{-2}s^{-1}$
368	0.075	< 0.25	11.1	$3.01x10^{-6}$	$13.36x10^{-6}$
184	0.075	< 0.25	11.1	$2.07x10^{-6}$	$9.19x10^{-6}$
92	0.075	< 0.25	11.1	$1.43x10^{-6}$	$6.35x10^{-6}$
46	0.075	< 0.25	11.1	$0.98x10^{-6}$	$4.35x10^{-6}$
23	0.075	< 0.25	11.1	$0.77x10^{-6}$	$3.42x10^{-6}$
11.5	0.075	< 0.25	11.1	$0.50x10^{-6}$	$2.22x10^{-6}$
5.7	0.075	< 0.25	11.1	$0.33x10^{-6}$	$1.47x10^{-6}$
46	0.0375	< 0.25	11.1	$0.55x10^{-6}$	$4.89x10^{-6}$
23	0.0375	< 0.25	11.1	$0.50x10^{-6}$	$4.44x10^{-6}$
11.5	0.0375	< 0.25	11.1	$0.14x10^{-6}$	$1.24x10^{-6}$
400	0.075	0.5	11.1	$3.10x10^{-6}$	$13.76x10^{-6}$
250	0.075	0.5	11.1	$2.90x10^{-6}$	$12.88x10^{-6}$
63	0.075	0.5	10.1	$1.58x10^{-6}$	$7.02x10^{-6}$
12.5	0.075	0.5	10.1	$0.80x10^{-6}$	$3.55x10^{-6}$
2.5	0.075	0.5	10.1	$0.43x10^{-6}$	$1.91x10^{-6}$
0.83	0.075	0.5	10.1	$0.30x10^{-6}$	$1.33x10^{-6}$

Open to air $[O_2]$ = 0.25 mM, I < 0.25 indicates natural ionic strength,
I = 0.5 adjusted using sodium nitrate, particle size 20 nm.

McCarthy et al. (1998) noted that the dissolution of dilute colloidal gold dispersions in aerated solutions follows the kinetics of a typical electrochemical process described by the mixed potential theory. However, they noted that due to the enhanced mass transfer of oxygen to the small colloidal particles (20 nm), the dissolution of unstabilized colloids occurs in the passive region of the anodic process. In contrast, the dissolution of gelatine stabilized colloids in solutions of high cyanide concentration is likely to occur in the active region (McCarthy et al., 1998). Therefore, it is important to compare and contrast the

results obtained using colloidal gold (unstabilized or gelatine stabilized) in thiosulfate solutions with the results for massive gold reported in the literature.

6.5 Initial rates of gold, silver and gold-silver alloys in thiosulfate solutions

Most of the rate data for thiosulfate leaching of massive gold under controlled hydrodynamic conditions (rotating discs) reported by Jeffrey (2001) are based on the dissolution of a gold-silver alloy (5%Ag) rather than pure gold. Therefore, the rates of dissolution of silver and gold-silver alloy reported in the literature are compared with the rate of dissolution of gold colloids in the absence or presence of silver colloids or silver nitrate determined in this study. A comparison is also made with the recently reported rate data (Zhang and Nicol, 2003, 2005) for the anodic dissolution of impurity-free gold in non-ammoniacal-, non-copper, as well as ammoniacal-copper(II)-thiosulfate solutions.

The Levich equation (Eq. 6.12) has been widely used for the interpretation of rate data (R_M, mol $m^{-2}s^{-1}$) based on the electrochemical or chemical dissolution of metal from a rotating disc under diffusion controlled conditions (Jeffrey, 2001):

$$R_M = J_X = 0.62 D_X^{\,2/3} \upsilon^{-1/6} C_X \omega^{1/2} \tag{6.12}$$

$$\log R_M = \log(C_X \omega^{1/2}) + \log(0.62 D_X^{\,2/3} \upsilon^{-1/6}) \tag{6.13}$$

$$D_X = \left[\left(\frac{\upsilon^{1/6}}{0.62} \right) C_X \omega^{1/2} \right]^{3/2} \tag{6.14}$$

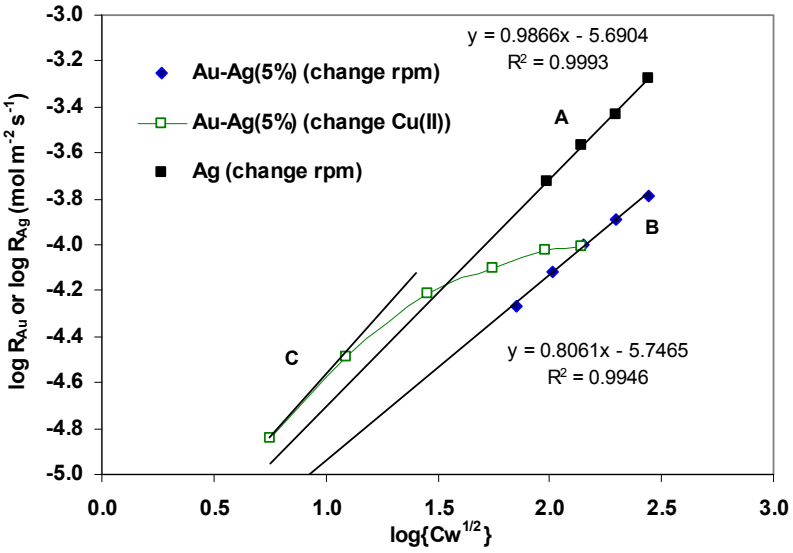
The Levich equation relates the two important variables rotation rate (ω, s^{-1}) and the concentration of the species X (C_X, mol m^{-3}) to R_M (mol m^{-2} s^{-1}), where the rate of diffusion of X (X = Cu(II)) to the gold surface is considered equal to the rate of a surface reaction at steady state. Other terms in Eq. 6.12 represent: J_X = flux of X (mol m^{-2} s^{-1}), and υ = kinematic viscosity (m^{-2} s^{-1}). The rate data can be analysed on the basis of Eq. 6.1. This in turn is useful in the discussion of the surface chemical reaction mechanism.

For example, Jeffrey (2001) reported the effect of rotation speed and copper(II) concentration on the initial rate of dissolution of gold-silver (5%) alloy and pure silver measured in solutions of copper(II)-ammonia-thiosulfate maintained at 30^{o}C using rotating electrode quartz crystal microbalance (REQCM). He noted that the initial concentration of copper(II) ions is lower than that of thiosulfate ([Cu(II)]/[$S_2O_3^{2-}$] =1/16), and thus, the flux of cupric tetraammine is expected to be the lowest. Fig. 6.9a shows a log-log plot of R_M as a function of $C_X \omega^{1/2}$ for M= Ag and Au and X = Cu(II) based on Jeffrey's results to examine the validity of Eq. 6.13. The linear relationship of slope ≈1 for silver in Fig. 6.9a shows the applicability of the Levich equation. The slope of line A in Fig. 6.9b (4x 10^{-6}) when substituted in Equation 6.12, along with the reported value of u=8.9x 10^{-7} m^{-2} s^{-1} (Jeffrey, 2001), gives the value of $D_{Cu(II)}$ = 5.0 x 10^{-10} m^{-2} s^{-1} at 30^{o}C. This value is consistent with $D_{Cu(II)}$ = 4.6 x 10^{-10} m^{-2} s^{-1} of cupric tetraammine ion based on the diffusion limiting current reported by Jeffrey (2001) and Nicol (1975) at ambient temperatures.

Thus, it is clear that the dissolution of silver by copper(II) is predominantly controlled by the diffusion of reactant and the rate of silver dissolution is equal to the rate of copper(II) diffusion to the surface.

The effect of copper(II) concentration on the rate of gold dissolution is shown in curve C of Fig. 6.9b. The initial linear relationship coinciding with line A at low copper(II) concentrations in the range 1-5 mM shows the applicability of the Levich equation. However, the slope of curve C approaches zero at higher copper(II) concentrations. Likewise, the slope of line B (1×10^{-6}), which is lower than that of line A, also decreases with increasing rotation speed indicating the non-validity of the Levich equation. Jeffrey (2001) concluded that the rate of gold dissolution from Au-Ag(5%) alloy is controlled by the rate of copper(II) diffusion to the surface at low concentrations (< 5 mM Cu(II)), but limited by a slow surface reaction at high concentrations.

(a)



(b)

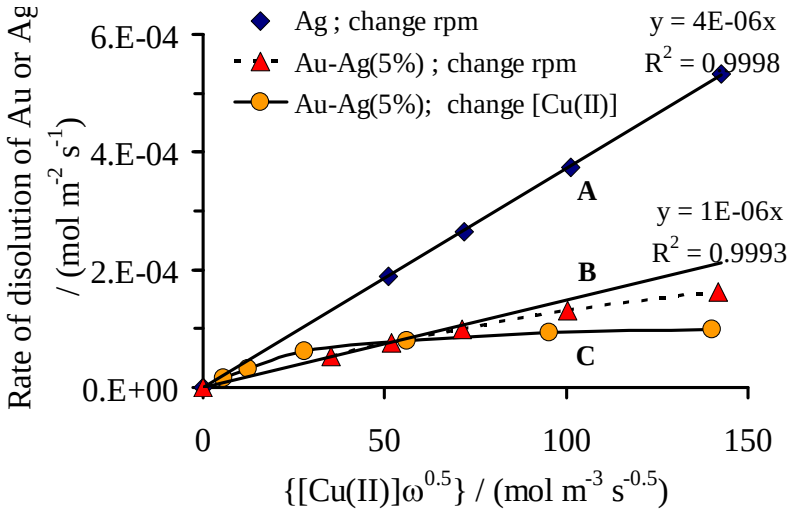


Fig. 6.9. *Effect of copper(II) concentration or rotation speed on the rate of dissolution of silver and gold-silver (5%) alloy: 30°C, 0.84 M ammonia, 0.4 M thiosulfate, pH ≈ 10 (Data from Jeffrey, 2001).*

The calculated reaction rate based on thiosulfate diffusion is also 30 times faster than the limiting rate of gold dissolution at high copper(II) concentrations shown in curve C (Jeffrey, 2001). This means that despite the decrease in copper(II) concentration due to the reaction with thiosulfate ions, a fraction of copper(II) and thiosulfate which arrive at the gold surface leave the surface unreacted (Jeffrey, 2001). In other words, the surface reaction is slower than the rate of diffusion of copper(II) and thus chemically controlled. This will be further examined for gold colloids by considering the effect of temperature and the activation energy based on the Arrhenious equation in Section 6.7.

6.6 Comparison with literature data

Table 6.5 shows that the rate of dissolution of gold powders and unstabilized colloidal gold in ammoniacal copper(II) thiosulfate solutions is of the same order (2.2 x 10^{-7} – 9.3 x10^{-7} mol m^{-2} s^{-1}), despite the large difference between particle sizes in the range 32 - 7250 nm. At a given particle size of ~ 30 nm, the rate is approximately halved (from 2.2 x 10^{-7} mol m^{-2} s^{-1} to 1.0 x 10^{-7} mol m^{-2} s^{-1}) in the presence of gelatine. The rate of dissolution of gold-silver alloy reported by Jeffrey (2001) shown in Fig. 6.9 (1.4 x 10^{-5} to 10 x10^{-5} mol m^{-2} s^{-1}) is two orders of magnitude higher than the rate of dissolution of pure gold (2.2 x 10^{-7} – 9.3 x10^{-7} mol m^{-2} s^{-1}) measured in this work and reported in Table 6.5. This is consistent with the results listed in Table 6.5, which show that the presence of silver colloids or silver nitrate enhance the rate of dissolution of gold colloids as a result of the catalytic effect of silver on gold dissolution. In the case of gold

powder of 2250 nm, the presence of 0.05 mM $AgNO_3$ causes an eight fold increase in rate from 4.7 to 37.5 mol m^{-2} s^{-1}.

Table 6.6 compares the rate of dissolution of massive gold based on chemical dissolution or mixed currents (Zhang and Nicol, 2003; 2005; Jiang et al., 1993a) with rate based on colloidal gold measured in this study. The increase in pH above 9.6 causes no significant effect on rate. There is reasonable agreement between the three sets of data. The differences can be related to the differences in surface roughness factor.

Table 6.5 *Effect of the type of gold and additives on the initial rate of dissolution*

Type of gold	Additive	Particle size (nm)	10^4 R_i (mM/min)	10^7 R_i (mol $m^{-2}s^{-1}$)
Powder	none	2250 7250	0.75 0.46	4.7 9.3
Colloid (unstabilized)	none	10 32	164 25	4.7 2.2
Colloid (gelatine stabilized)	none	16 20 25 30	22 20 13 12	1.0 1.1 0.9 1.0
Colloid (gelatine stabilized)	None 0.10 mM Ag(c) 0.05 mM $AgNO_3$ 0.15 mM $AgNO_3$	20	13 23 16 42	0.7 1.3 0.9 2.3
Powder	None 0.05 mM $AgNO_3$	2250	0.75 6.0	4.7 37.5

Conditions: 25°C, pH 9.5, 1.5 mM Cu(II), 20 mM $Na_2S_2O_3$, 120 mM NH_3+NH_4^+.

Table 6.6 *Comparison of rate data for massive gold and colloidal gold at 25 °C*

Gold	$[S_2O_3^{2-}]$ (M)	$[NH_3+NH_4^+]$ (M)	Cu(II) (mM)	pH	10^7 R (mol m^{-2} s^{-1})
Rotating disc (Zhang & Nicol, 2003)					
	0.1	0	0	a	0.6
	1	0	0	a	17
	1	0	0	10.6[b]	7.0
	1	0.2	0	10.6[b]	14
	0	0.2	0	10.6[b]	<0.1
Anode (Jiang et al.,1993a)					
	1	c	1	10	0.6[c]
Powder (This work Table 6.5)					
	0.02	0.12	1.5	9.5	5-9[d]
Unstabilized Colloid					
	0.02	0.12	1.5	9.5	2-5[e]
Gelatine stabilized Colloid (This work)					
	0.02	0.12	1.5	9.3	1.1
	0.04	0.24	2.0	9.3	1.7
	0.04	0.24	2.0	9.6	1.8
	0.04	0.24	2.0	10.0	.8
	0.04	0.24	2.0	11.0	1.7

a. 0.1 M NaOH.

b. pH adjusted with NaOH.

c. Based on corrosion current Cu(II) = $Cu(NH_3)_4^{2+}$, 20 °C.

d. Particle size 2250-7250 nm.

e. Particle size 10-32 nm.

6.7 Effect of temperature on initial rate

Figure 6.10 shows the effect of temperature on initial rate and the percentage of gold dissolution in oxygenated ammoniacal thiosulfate or oxygen-free copper(II)-ammonia-thiosulfate systems after 2 hours or 5 hours, based on the rate data listed in Appendix 2 (Table A2.5). The effect of temperature on rates was much larger in the copper(II)-ammonia-thiosulfate system than that in the oxygen-ammonia-thiosulfate system. The lowest temperature used by other researchers was 30^{o}C (Jeffrey, 2001), 50^{o}C (Li and Kuang, 1998) and 60^{o}C (Cao et al., 1992; Ji and Yu 1991), compared with 22^{o}C or 25^{o}C used in the present study. The Arrhenius plots of ln (R_i) versus 1/T shown in Fig. 6.11 gave slopes corresponding to activation energies of 40 kJ mol^{-1} and 25 kJ mol^{-1} for the oxidation of gold by copper(II) and oxygen respectively.

The decrease in copper(II) concentration with time was faster at higher temperatures, as noted in Chapter 4, and this can also affect the rates. Thus, the rates of gold oxidation interpolated at the same residual copper(II) concentration of 1.75 mM are shown in the Arrhenius plot in Fig. 6.12. The slope corresponds to an activation energy of 50 kJ mol^{-1} for oxidation of gold by copper(II). It is reasonable to conclude that the dissolution of gold colloids by copper(II) is controlled by the rate of the surface chemical reaction. This is consistent with the discussion based on the Levich equation presented in Section 6.5.

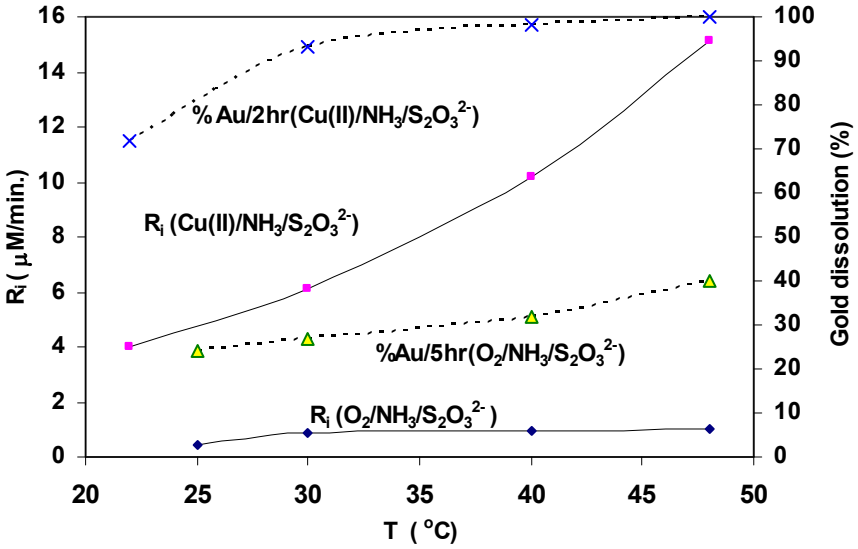


Fig. 6.10 *Effect of temperature on initial rate and final gold dissolution.*

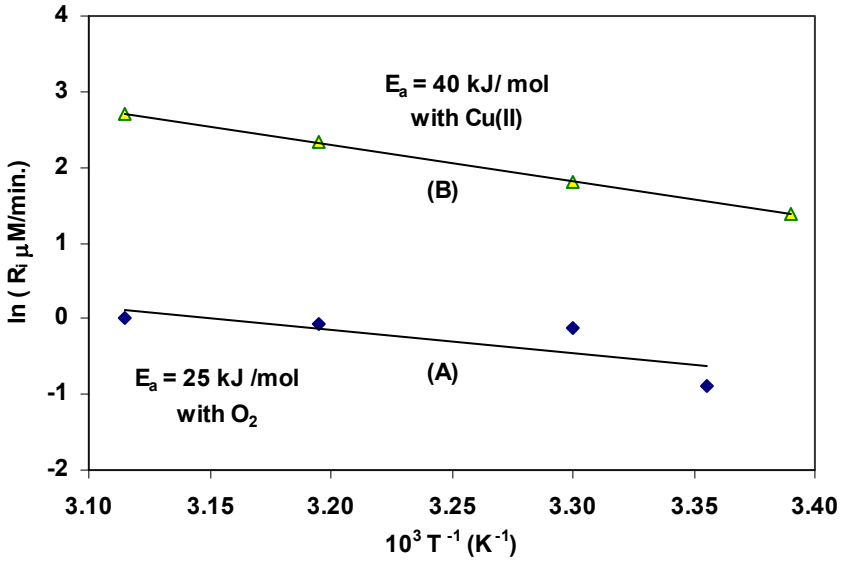


Fig. 6.11 *Arrhenius plots based on initial rates.*

(A): [O_2] = 0.56 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

(B): [Cu(II)] = 2.0 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.

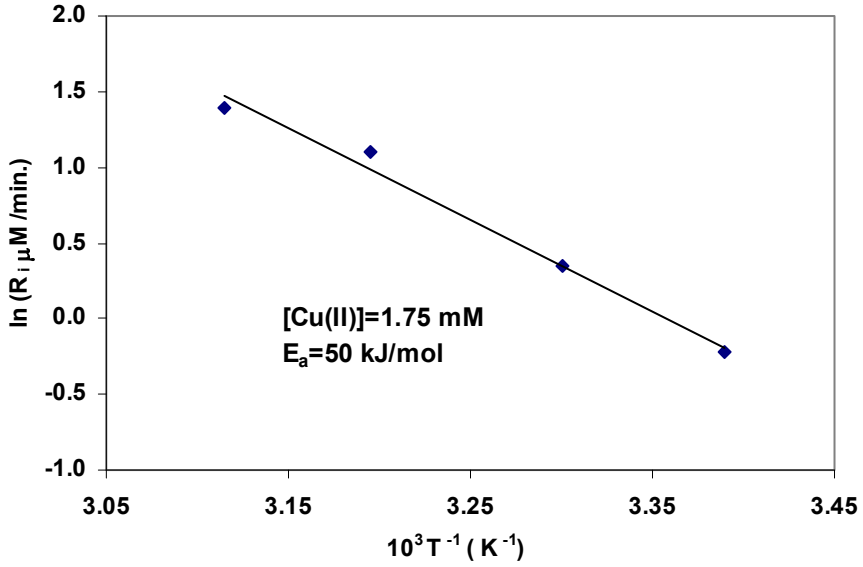


Fig. 6.12 *Arrhenius plots based on initial rates at a residual copper(II) concentration of 1.75 mM. (Initial conditions as in Fig. 6.11B).*

6.8 Dissolution of gold in the absence of copper(II)

6.8.1 Effect of oxygen concentration

Ji et al. (2003) reported the positive effect of increased oxygen pressure on the rate of gold leaching in oxygenated thiosulfate media at elevated temperatures in the absence of both copper(II) and ammonia. For example, the increase in oxygen pressure from 30 psig to 100 psig, at 60^{o}C and pH 11 increased gold extraction in the first 20 minutes from 50% to 56%. The results obtained in the present study (Table 6.7) show that an increase in dissolved oxygen concentration in the absence of ammonia had no effect on initial rates. In contrast, an increase in dissolved oxygen concentration at constant ammonia and thiosulfate concentrations had a positive effect on initial rates. Quantitative analysis of these results will be described later.

Table 6.7 *Effect of oxygen on the initial rate of gold dissolution*

$[O_2]$ (mM)	$[NH_3+NH_4^+]$ (mM)	R_i (μM/min.)
0.25	0	2.1
0.75	0	2.1
0.06	240	0.6
0.25	240	0.9
0.50	240	1.1
0.75	240	1.2

$[Na_2S_2O_3]$ = 50 mM, pH 9.3 at 25°C.

6.8.2 Effect of ligand concentration

Previous studies have shown that the passivation of gold by a surface film (sulfur) in thiosulfate solutions is minimised in the presence of ammonia. Thus, the electrochemical rate of gold oxidation in different electrolyte solutions follows the order NH_3-$(NH_4)_2SO_4$ < $Na_2S_2O_3$ < $Na_2S_2O_3$-NH_3-$(NH_4)_2SO_4$ (Zhang and Nicol, 2003), while gold oxidation in oxygen saturated solutions follows the order O_2-$Na_2S_2O_3$ < O_2-$(NH_4)_2S_2O_3$ (Chandra and Jeffrey, 2003). Furthermore, the electrochemical rate of gold dissolution increases with the increase in thiosulfate concentration from 0.1 M to 1.0 M (Zhang and Nicol, 2003, Table 6.6).

Figure 6.13 shows the initial rates of gold dissolution obtained in the present study (summarized in Appendix A2, Table A2.1) to illustrate the effects of

(i) increasing total ammonia or thiosulfate (C and F),

(ii) increasing ammonia in the presence of 20 mM $Na_2S_2O_3$ (D), and

(iii) increasing thiosulfate in the presence of 200 mM NH_3 (E).

The rates shown in the different curves follow the order C ≤ D ≤ E < F. Thus, the initial rates of gold oxidation by 0.25 mM O_2 in different systems follow the order NH_3 < (NH_3 + $Na_2S_2O_3$) < $Na_2S_2O_3$.

Figure 6.14 plots percentage gold dissolution versus R_i to examine whether a higher initial rate necessarily means a higher extent of gold dissolution over several hours. Although R_i was higher in thiosulfate solutions in the absence of ammonia (Fig. 6.13), thiosulfate alone gives a low gold dissolution (line F, Fig. 6.14). In the absence of ammonia, thiosulfate decomposes when in contact with gold at an open circuit potential, leaving a film of several sulfur-containing species, which blocks the electrode (Pedraza et al., 1988; Zhang and Nicol, 2003). So, despite the fast initial rate in a solution of thiosulfate alone (line F), the extent of gold dissolution was lower than that obtained in the presence of ammonia. This highlights the role of ammonia in removing the surface (sulfur) film on gold as described by Zhang and Nicol (2003), and the beneficial effect of mixed-ligands on the extent of gold dissolution. In the lixiviant system of oxygen-thiosulfate-ammonia, the role of ammonia is proposed to be the removal/prevention of surface sulfur film. The initial rate was enhanced by the increase in ammonia concentration in the absence of thiosulfate solutions and was independent of ammonia at higher concentrations (line C, Fig. 6.13). However, the overall extent of gold dissolution remained very low (line C, Fig. 6.14). This may be related to the disproportionation or oxidation of gold(I) noted in Eqs. 5.12 - 5.13. The initial rates were higher in lower ammonia concentration in the presence of thiosulfate solutions (line D, Fig. 6.13), despite

lower gold electrode potential. However, the overall extent of gold dissolution was lower (line D, Fig. 6.14).

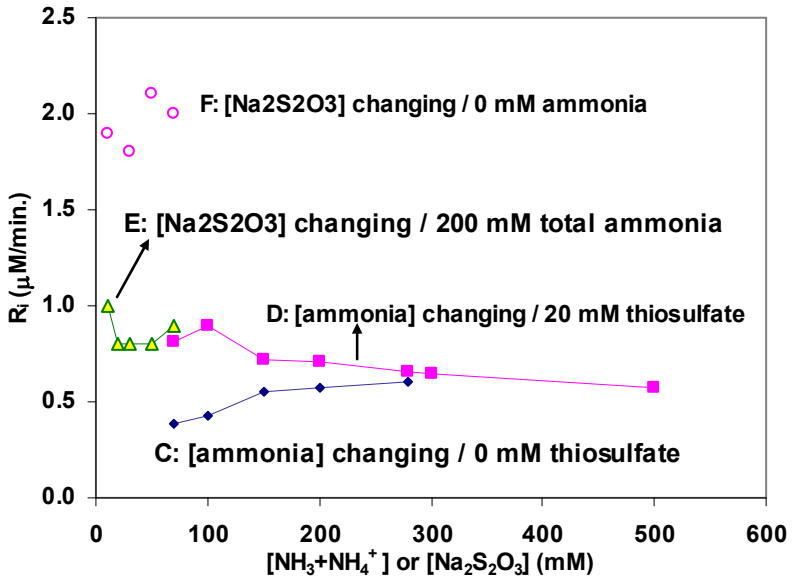


Fig. 6.13 *Effect of ammonia and thiosulfate on initial rates of gold dissolution by oxygen.*

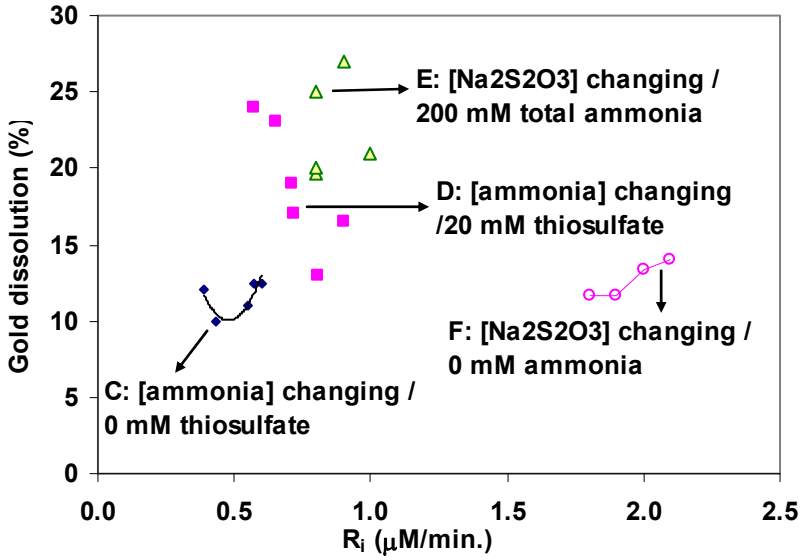


Fig. 6.14 *Comparison between initial rates and final gold dissolution. Initial rates from Fig. 6.13, gold dissolution percentage after 5 hours, $[O_2]$ = 0.25 mM, pH = 9.5; initial [Au(c)] = 0.1 mM at 25°C.*

Although the initial rate of dissolution decreased with increasing ammonia concentration in the presence of thiosulfate (line D in Fig. 6.13), the extent of gold dissolution was higher at low initial rates (line D in Fig. 6.14). Moreover, the initial rate in thiosulfate in the absence of ammonia (line F) was twice that observed in ammonia-thiosulfate mixtures (line E, line D). This behaviour differs from the anodic or chemical dissolution of massive gold reported by Zhang and Nicol (2003) and Chandra and Jeffrey (2003). As shown in Table 6.8, the rate of gold oxidation in mixed ammonia-thiosulfate system was greater than that in a pure thiosulfate system.

Table 6.8 *Effect of ammonia and thiosulfate on dissolution rate of massive gold*

Gold	$[Na_2S_2O_3]$ (M)	$[NH_3+NH_4^+]$ (M)	[Cu(II)] (mM)	pH	10^7 R (mol m^{-2} s^{-1})
Non-oxygenated solutions (Zhang & Nicol, 2003)					
Gold disc	1	0	0	10.6[a]	7
	1	0.2	0	10.6	14
	0	0.2	0	10.6	<0.1
Oxygenated solutions (Chandra and Jeffrey, 2003)					
Au(5% Ag)[b]	0.2	0	0		1
	0.2	0.4	0		40[c]
	0.2	0.4	0		31[d]

a. pH adjusted with NaOH.

b. Gold-silver alloy, solution saturated with oxygen, pH not reported.

c. Based on corrosion current.

d. Based on chemical dissolution (REQCM)

6.8.3 Effect of chloride concentration

Figure 6.15 shows that in ammonia alone, the effect of sodium chloride on R_i was insignificant (line b). However, in thiosulfate or mixed ammonia-thiosulfate solutions the highest dissolution rate was observed in the presence of 0.2 M NaCl. Catalytic effect of chloride is greater with oxygen-thiosulfate solution than with ammonia-thiosulfate solution; effect of chloride on surface film may be the cause. Moreover, in thiosulfate or mixed ammonia-thiosulfate solutions, the extent of gold dissolution (after 3 hours) increased with increasing R_i (lines a, c Fig. 6.16). This shows the involvement of chloride ions in the surface reaction, as described later.

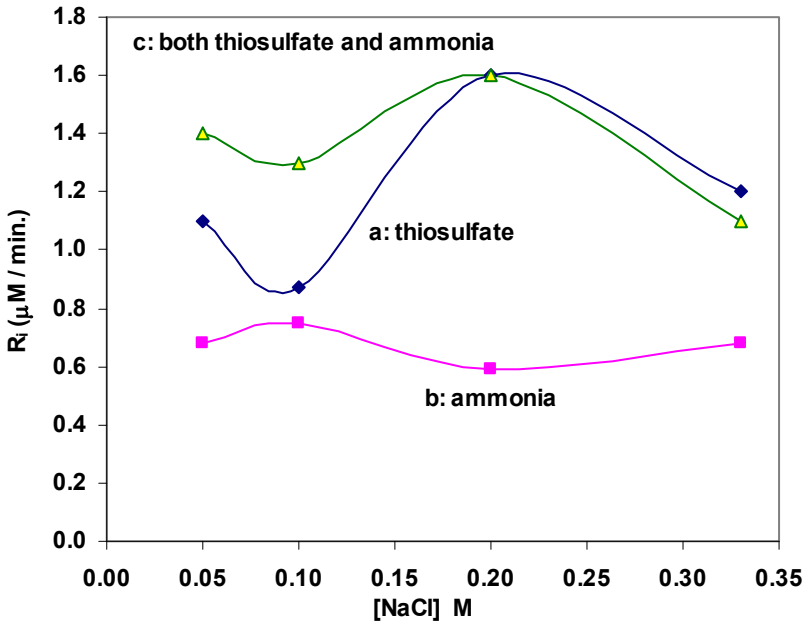


Fig. 6.15 *Effect of chloride on initial rates and final gold dissolution by oxygen. pH 9.5 and 0.25 mM O_2.*

a: $[Na_2S_2O_3]$ = 30 mM, $[NH_3 + NH_4^+]$ = 0 mM.

b: $[Na_2S_2O_3]$ = 0 mM, $[NH_3 + NH_4^+]$ = 120 mM.

c: $[Na_2S_2O_3]$ = 20 mM, $[NH_3 + NH_4^+]$ = 120 mM.

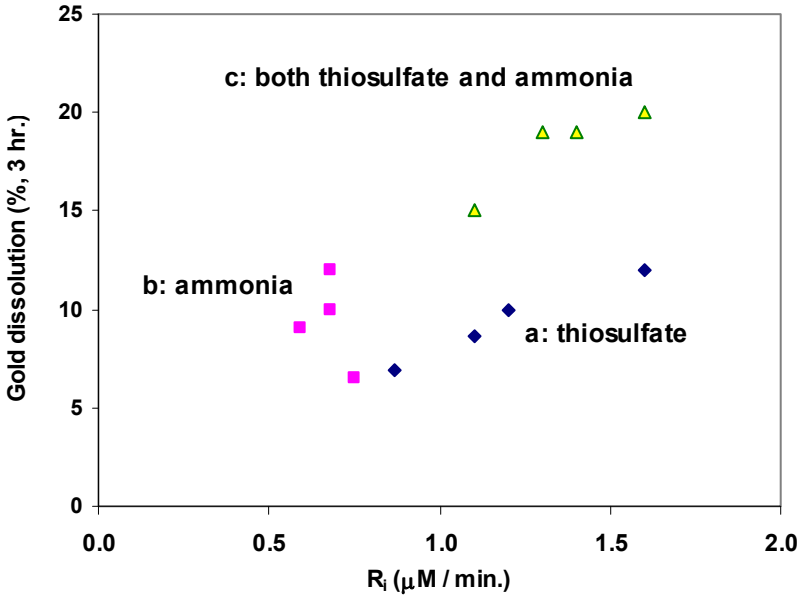


Fig. 6.16 *Comparison between initial rates and final gold dissolution by oxygen. Initial rates from Fig. 6.15, gold dissolution percentage after 3 hours, pH 9.5 and 0.25 mM O_2, [NaCl]: 0.05 M – 0.33 M.*

a: $[Na_2S_2O_3]$ = 30 mM, $[NH_3 + NH_4^+]$ = 0 mM.

b: $[Na_2S_2O_3]$ = 0 mM, $[NH_3 + NH_4^+]$ = 120 mM.

c: $[Na_2S_2O_3]$ = 20 mM, $[NH_3 + NH_4^+]$ = 120 mM.

6.9 Dissolution of gold in anaerobic copper(II) solutions

6.9.1 Effect of reagent concentration and pH

Without thiosulfate, the dissolution of gold colloid in copper(II)-ammonia solution was very slow (Fig. 6.17). The initial rates with different initial concentrations of copper(II) were 0.3 or 0.4 μM /min. However, in the presence of thiosulfate, the initial rate was higher (2.3 μM/min) and increased dramatically with increasing initial copper(II) concentration.

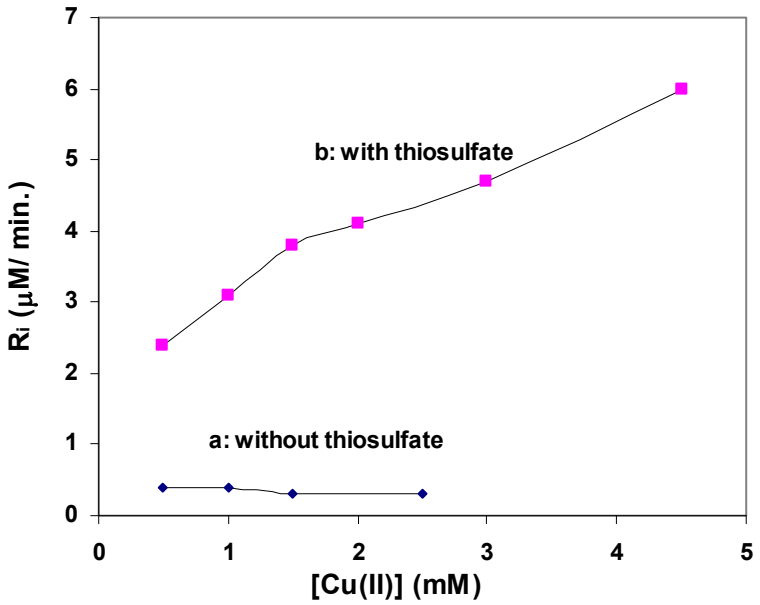


Fig. 6.17 *Effect of copper(II) on initial rate of gold dissolution under nitrogen.*
a: $[Na_2S_2O_3]$ = 0 mM, $[NH_3+NH_4^+]$ = 120 mM, pH 9.5.
b: $[Na_2S_2O_3]$ = 50 mM, $[NH_3+NH_4^+]$ = 240 mM, pH 9.3.
(Appendix A2.2).

As shown in Fig. 6.18, the effect of ammonia concentration on R_i in the absence of thiosulfate was negligibly small (line a). The increase in concentration of

either of the ligands in the mixed ammonia-thiosulfate ligand system caused an increase in R_i (line c or b). However, the effect of thiosulfate concentration on R_i was much larger than that of ammonia at a given concentration (line c versus b).

At higher concentrations, the effect of thiosulfate on R_i became less significant. Likewise, an increase in ammonia concentration beyond 200 mM has no significant effect on the initial rate of gold dissolution. An increase in pH (Fig. 6.19) showed the same effect on R_i as that of ammonia (Fig. 6.18). Thus, a higher concentration of total ammonia at a constant pH of 9.3 as well as a higher pH at a constant total ammonia concentration of 240 mM had a negligible or slightly detrimental effect on the initial rate of gold dissolution. These results are consistent with the data reported by Jeffrey (2001), based on the rate of massive gold-silver alloy (5% Ag) dissolution. The measured rate using a rotating electrode quartz crystal microbalance showed that the increase in ammonia concentration beyond 0.4 M retarded the gold oxidation by copper(II). Moreover, these results are also consistent with literature information described on page 59 and summarised in Table 2.12.

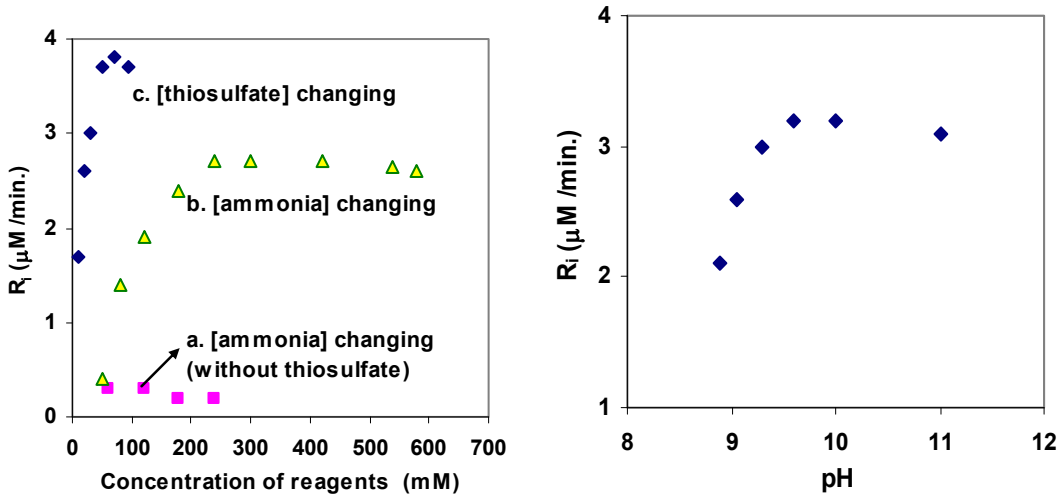


Fig. 6.18 *Effect of ammonia, thiosulfate and pH on initial rates of gold dissolution in copper(II) solutions under nitrogen.*

[Cu(II)]=1.5mM.

a: pH 9.5; [$Na_2S_2O_3$] = 0 mM

b: [$Na_2S_2O_3$] = 20 mM, pH 9.3;

c: [NH_3+NH_4^+] = 240 mM, pH 9.3.

Fig. 6.19 *Effect of pH on initial rates of gold dissolution in copper-ammonia-thiosulfate solutions under nitrogen.*

[Cu(II)]=2.0 mM, [$Na_2S_2O_3$] = 40 mM, [NH_3+NH_4^+] = 240 mM.

6.9.2 Effects of background salts

Breuer and Jeffrey (2003b) noted that sulfate ions combine with copper(II) to form the complex species $Cu(NH_3)_p(SO_4)^0$, and that thiosulfate must displace sulfate before it can react with copper(II) (Eq. 6.15).

$$Cu(NH_3)_p(S_2O_3)^0 + SO_4^{2-} = Cu(NH_3)_p(SO_4)^0 + S_2O_3^{2-} \quad (6.15)$$

Therefore, the addition of sodium sulfate can decrease copper(II) reduction and gold oxidation (Chu et al., 2003). The addition of sodium nitrate instead of sodium sulfate can slightly increase the rate of copper(II) reduction, while addition of chloride is reported to be beneficial for gold oxidation (Li and Kuang, 1998; Chandra and Jeffrey, 2004).

Figures 6.20 - 6.21 compare and contrast the effect of sodium salts (sulfate and chloride) on initial rates, and concentration of residual copper(II) after 10 minutes. In this study, high ionic strength of sodium sulfate caused an increase in residual copper(II) concentration in thiosulfate solutions during the first 10 minutes. This in turn was responsible for the beneficial effect of sodium sulfate on R_i and the extent of gold dissolution (Fig. 6.20).

Figure 6.21 shows the effect of sodium chloride concentration on the initial rates and residual copper(II) after 10 minutes. It also shows the results obtained in the absence of thiosulfate reagent. It can be seen that the presence of sodium chloride does not significantly affect the residual copper(II) concentration in the

presence or absence of thiosulfate. However, the increase in sodium chloride concentration increases the initial rate in both cases. This indicates the involvement of chloride ion as a catalyst in the surface reaction of gold with copper(II), this may be due to effect of chloride ions on surface film and/or affecting copper(II) activity, both via the formation of mixed complexes.

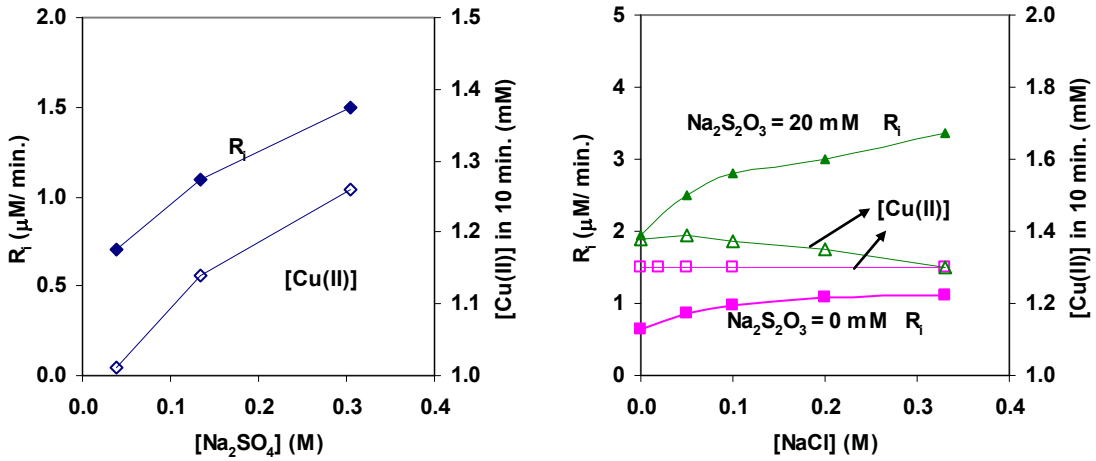


Fig. 6.20 *Effect of sulfate on initial rate of gold dissolution and residual copper(II) in ammonia-thiosulfate solutions under nitrogen.*
$[Cu(II)]_i$ =1.5 mM, $[Na_2S_2O_3]$ = 10 mM, $[NH_3+NH_4^+]$ = 60 mM, pH 9.5

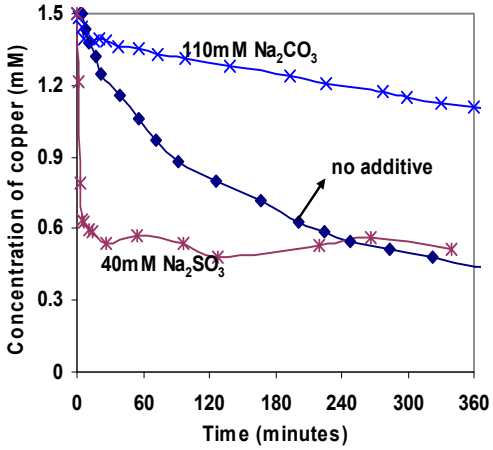
Fig. 6.21 *Effect of chloride on initial rate of gold dissolution and residual copper(II) in ammonia solutions under nitrogen.*
$[Cu(II)]_i$ =1.5 mM, $[NH_3+NH_4^+]$ = 120 mM, pH 9.5.

The addition of sodium carbonate led to the maintenance of a higher residual copper(II) concentration and a higher E_H (Figs. 6.22, 6.23). However, the gold dissolution during the first 5 hours was lower than that in the absence of sodium carbonate (Fig. 6.24). In contrast, the addition of sodium sulfite decreased the residual copper(II), E_H and the overall percentage of gold dissolution (Figs. 6.22-6.24). These observations may be related to the decrease in concentration of $Cu(NH_3)_p(S_2O_3)^0$ according to Eqs. 6.16 and 6.17. Further degradation of

$Cu(NH_3)_p(SO_3)^0$ to Cu(I), dithionate, and eventually to sulfate explains the large decrease in gold dissolution in the presence of sodium sulfite, compared to that observed in the absence of additives (Fig. 6.24).

$$Cu(NH_3)_p(S_2O_3)^0 + CO_3^{2-} = Cu(NH_3)_p(CO_3)^0 + S_2O_3^{2-} \quad (6.16)$$

$$Cu(NH_3)_p(S_2O_3)^0 + SO_3^{2-} = Cu(NH_3)_p(SO_3)^0 + S_2O_3^{2-} \quad (6.17)$$



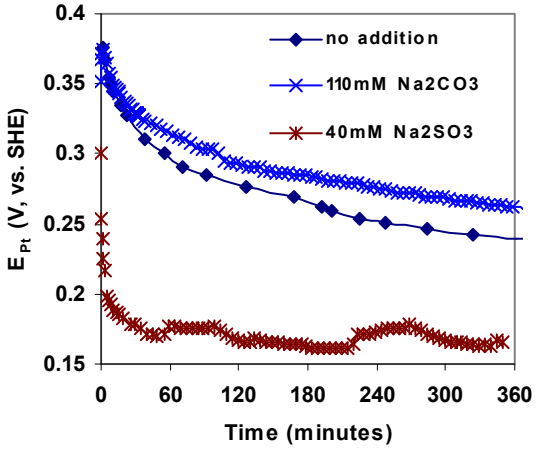


Fig. 6.22 *Effect of sulfite or carbonate on residual copper(II) in ammonia-thiosulfate solution under nitrogen.*

Fig. 6.23 *Effect of sulfite or carbonate on potential of platinum electrode under nitrogen.*

$[Cu(II)]_i$ =1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH 9.5

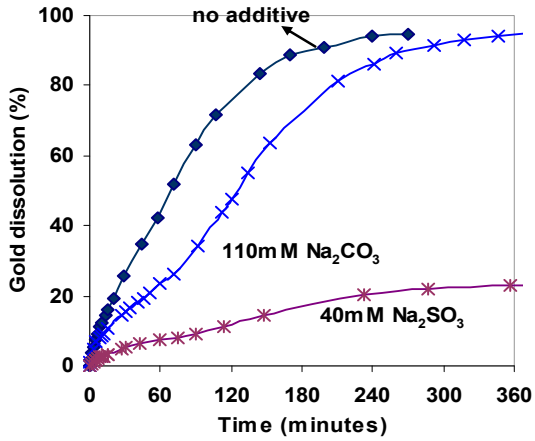


Fig. 6.24. *Effect of sulfite or carbonate on gold dissolution in copper(II)-ammonia-thiosulfate solutions under nitrogen.*

$[Cu(II)]_i$ =1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH 9.5

The presence of chloride had a positive effect on the initial rate of gold dissolution in the absence of thiosulfate (Fig. 6.21), but no effect on the final extent of gold dissolution (13-14% after 6 hrs, Table 4.18). In comparison, both the initial rate and total dissolution after 2 hours were increased in the presence of thiosulfate (Figs. 6.25, 6.26). This is consistent with the previously published results (Li and Kuang, 1998; Chu et al., 2003).

Figures 6.25 and 6.26 show the effect of silver nitrate and sodium nitrate to compare the relative effects of silver(I), chloride, and nitrate ions. The effect of silver(I) on the initial rate was much larger than that of chloride (Fig. 6.25), but both silver(I) and chloride were equally beneficial for total gold dissolution (Fig. 6.26). Addition of $NaNO_3$ showed no effect on initial rate of gold dissolution (Fig. 6.25).

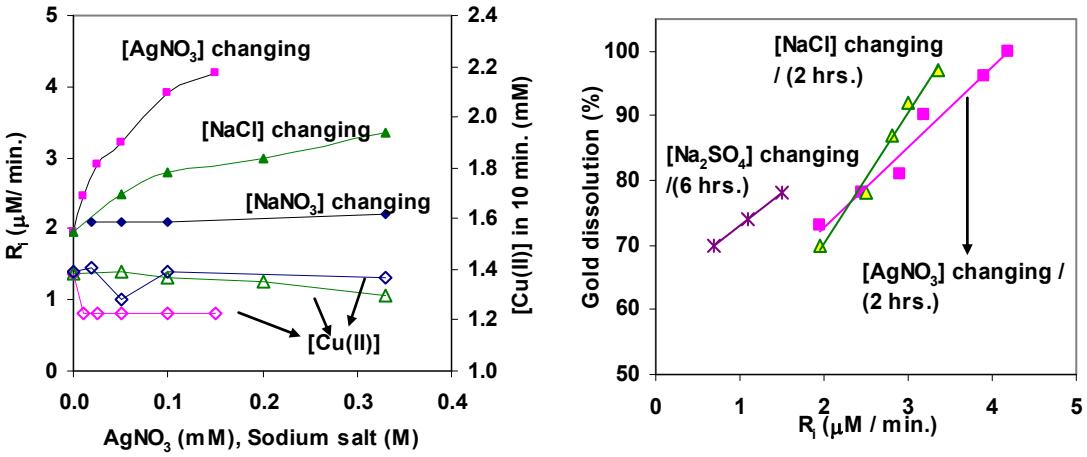


Fig. 6.25 *Effect of nitrate, chloride or silver(I) ions on initial rate of gold dissolution under nitrogen.*

Fig. 6.26 *Comparison between initial rates and final gold dissolution in the presence of chloride, nitrate or silver(I) under nitrogen. Initials rates from Fig. 6.25, [Cu(II)]=1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH 9.5.*

The relative magnitude of initial rate in the presence of three background salts $AgNO_3$ > NaCl > $NaNO_3$ follows an opposite trend to the residual copper(II) concentration measured after 10 minutes (Fig. 6.25). As previously noted, these results show the direct involvement of Ag(I) and Cl^- ions in the surface reaction, possible by interfering with a sulfur containing surface passivating film. It is important to establish a reaction scheme which gives a qualitative interpretation to some of these trends, while others need a quantitative treatment.

6.10 Dissolution of gold by oxygenated copper(II) solutions

6.10.1 The role of oxygen

The published results, based on both fundamentals and leaching studies, show the need for the presence of all four reagents: copper(II), oxygen, ammonia, and thiosulfate for the success of gold dissolution in thiosulfate media (Berezowski and Sefton, 1979; Jeffrey et al., 2003; Molleman and Dreisinger, 2002). In an experiment carried out in this study, the concentration of oxygen in a mixed ammoniacal copper(II)-thiosulfate solution open to air (without any bubbling of air or oxygen) decreased from 0.25 mM to 0.06 mM during the period of 15 minutes after mixing (Appendix A2, Table A2.4). This showed the consumption of oxygen by the copper(II) catalysed oxidation of thiosulfate as represented by the overall reactions in Eqs. 2.10a and 2.10b, leading to the production of sulfate and trithionate (Byerley et al., 1973a; 1975).

$$S_2O_3^{2-} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O \quad (2.10a)$$

$$1.5S_2O_3^{2-} + O_2 + 0.5H_2O = S_3O_6^{2-} + OH^- \quad (2.10b)$$

Results from previous studies described in Chapter 2 also showed that O_2, Cu(II) and O_2-Cu(II) mixed system, oxidized thiosulfate and gold. The relative rates followed the general order O_2 < Cu(II) < O_2-Cu(II). However, excess oxygen was detrimental for gold oxidation. The beneficial effect and detrimental effect of O_2 can be related to one or more of the following mechanisms:

Beneficial effects are caused by

(i) increase in copper(II) concentration due to oxidation of copper(I) by O_2 (Lam and Dreisinger, 2003; Wensveen and Nicol, 2005) and

(ii) direct oxidation of gold by oxygen.

Detrimental effects are caused by

(i) decrease in thiosulfate concentration due to copper(II) catalysed oxidation by oxygen (Byerley et al., 1975),

(ii) formation of ions such as $S_2O_5^{2-}$, which are detrimental to gold oxidation (Jeffrey et al., 2003), and

(iii) formation of polythionates and sulfate which may associate with $Cu(NH_3)_p^{2+}$, thus decreasing the concentration of the copper(II) species responsible for gold oxidation, $Cu(NH_3)_p(S_2O_3)^0$.

Thus, an attempt was made to compare the effect of concentration of copper(II), thiosulfate and oxygen on (i) residual copper(II), and (ii) initial rate and gold dissolution percentage, in order to clarify the role of oxygen.

6.10.2 Effect of initial copper(II) concentration

Figure 6.27 shows the effect of the initial concentration of copper(II) on initial rate in ammoniacal copper(II) thiosulfate solutions, in which the reagent concentrations were maintained at $[O_2]$ = 0 mM or 0.31 mM, $[Na_2S_2O_3]$ = 50 mM and $[NH_3 + NH_4^+]$ = 240 mM. It also shows the variation in residual copper(II) concentration after 10 minutes and compares the results with the effect of copper(II) concentration in the presence of nitrogen or oxygen. The lower values of R_i in oxygenated solutions are a result of lower concentrations of copper(II). Fig. 6.28 shows the variation in dissolution of gold after 3 h as a function of the initial copper(II) concentration in the two cases. Although the initial rate of dissolution was lower in oxygenated solutions (Fig. 6.27), the percentage of gold dissolution in 3 hours was higher than that in the absence of oxygen (under nitrogen, Fig. 6.28). These results also show the beneficial effect of oxygenation on gold dissolution by ammoniacal copper(II) thiosulfate solutions.

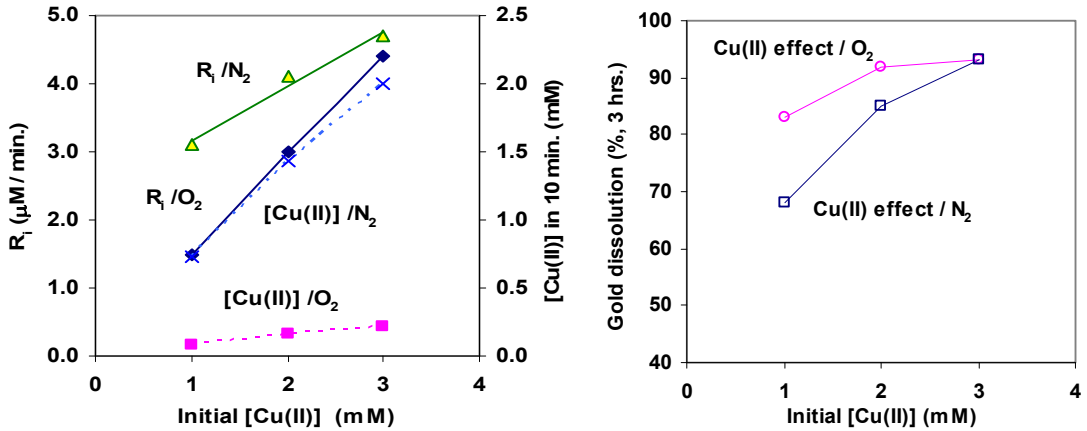


Fig. 6.27 *Effect of initial copper(II) on initial rate of gold dissolution and residual copper(II) concentration.*

Fig. 6.28 *Effect of initial copper(II) on final gold dissolution. $[Na_2S_2O_3]$ = 50 mM, $[NH_3+NH_4^+]$ = 240 mM, pH 9.3, $[O_2]$ = 0 (N_2) or 0.31 mM (based on the data reported in Appendices A 2.2, A 2.4).*

6.10.3 Effect of thiosulfate concentration

Figure 6.29 shows the effect of thiosulfate concentration on initial rates and residual copper(II) concentrations after 10 minutes in the presence or absence of oxygen. Fig. 6.30 shows percentage dissolution of gold colloid after 3 hours. The increase in thiosulfate concentration showed a beneficial effect on R_i in the absence of oxygen, but a detrimental effect in the presence of oxygen. However, in both cases the increase in thiosulfate concentration caused a decrease in residual copper(II) concentration. Oxygenation is beneficial on the initial rates at low thiosulfate concentrations (Fig. 6.29).

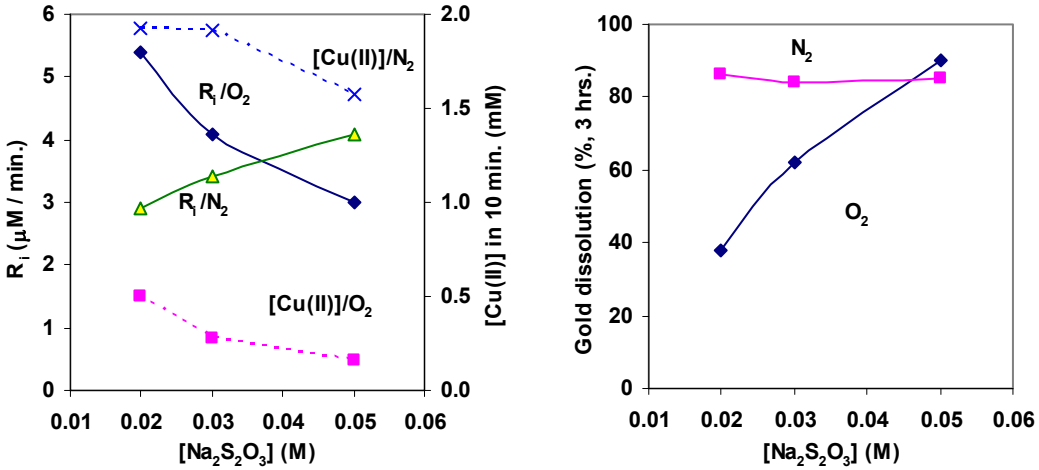


Fig. 6.29 *Effect of thiosulfate on initial rate of gold dissolution and residual copper(II) concentrations.*

Fig. 6.30 *Effect of thiosulfate on final gold dissolution.*
[Cu(II)] = 2.0 mM, $[NH_3+NH_4^+]$ = 240 mM, pH 9.3, $[O_2]$ = 0 or 0.31mM.

Fig. 6.30 shows a different trend from that observed in Fig. 6.28. In Fig. 6.28 the total gold dissolution increased with the increase in initial copper(II) concentration and R_i. However, as shown in Fig. 6.30, higher thiosulfate concentrations led to higher gold dissolution over 3 hours in the presence of oxygen, despite the lower initial rates. Molleman and Dreisinger (2002) noted that excessive oxygenation by forced aeration of the leach solution generated copper(II), which catalysed thiosulfate degradation and thus decreased gold extraction. This detrimental effect of oxygen is nullified in the presence of a high concentration of thiosulfate (Fig. 6.30).

6.10.4 Effect of oxygen concentration

Figure 6.31 shows the effect of oxygen concentration on R_i in the presence or absence of copper(II) in ammoniacal thiosulfate solutions. It is clear that the oxidation of gold with both copper(II) and oxygen was faster than that with oxygen alone. In the absence of copper(II), the increase in oxygen concentration had a positive effect on R_i (Fig. 6.31) and gold dissolution percentage (Fig. 6.32). Oxygen at low concentration had no significant effect on gold oxidation by copper(II). However, a high concentration of oxygen had a negative effect on R_i (Fig. 6.31) and percentage gold dissolution (Fig. 6.32). These observations are consistent with the results reported by Chu et al. (2003) summarised in Fig. 6.33.

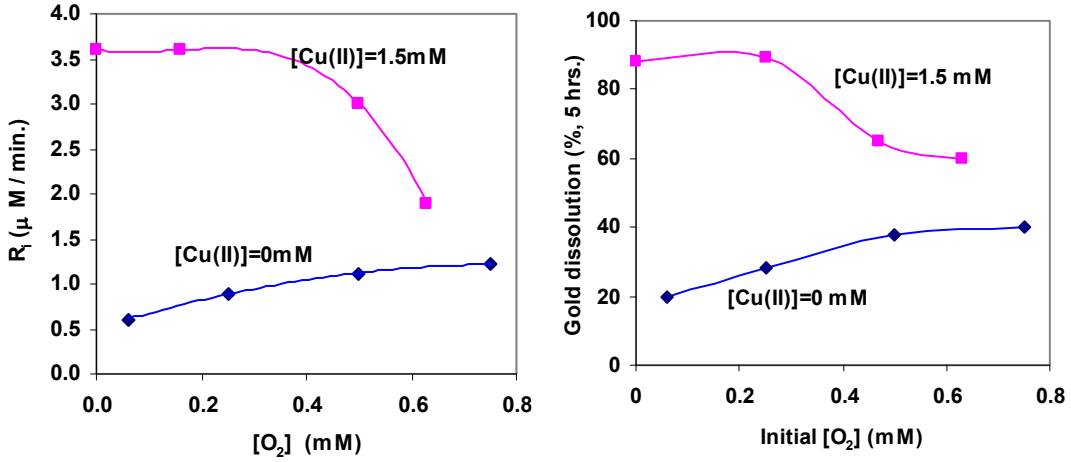


Fig. 6.31 *Effect of oxygen and copper(II) on initial rate of gold dissolution.*

Fig. 6.32 *Effect of oxygen and copper(II) on final gold dissolution.*

[$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH 9.5, 25ºC.

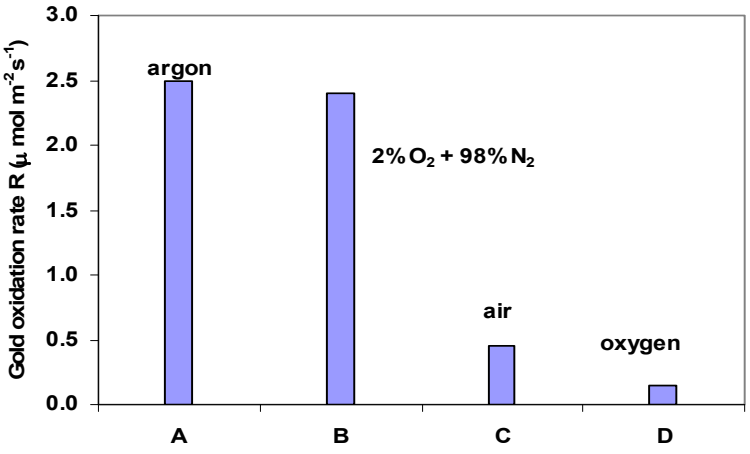


Fig. 6.33 *Effect of oxygen on the rate of gold oxidation by copper(II).*

Results based on REQCM (Chu et al., 2003).

[$Na_2S_2O_3$] = 50 mM, [NH_3 +NH_4^+] = 20 mM, pH 9.5, at 30ºC.

According to the results reported by Muir and Aylmore (2004) and Chu et al. (2003), the rate of thiosulfate oxidation in oxygenated copper(II)-ammonia solutions was faster than that of gold, leading to a decrease in thiosulfate concentration during reaction. For example, Table 6.9 shows that the rate of oxidation of thiosulfate was three orders of magnitude larger than that of gold (Muir and Aylmore 2002), as noted earlier in Eq. 6.1 (Section 6.3).

Table 6.9 *Comparison between oxidation rates of gold and thiosulfate*

$[CuSO_4]$ (mM)	$[NH_3+NH_4^+]$ (mM)	$[Na_2S_2O_3]$ (mM)	T ^oC	$[O_2]$ (mM)	Rate (μM/min.)		Refe-rence
					gold	thiosulfate	
1.9	200	50	ambient	0.16	0.01	50	a
2.0	200	100	30	1 l/min.		900	b
0.5	400	200	ambient	open to air		250	c
0	0	100	40	100 psig		50	d
0	0	50	25	0.75	2.1	10	e
1.5	240	50	25	0.5	3.0		f

a. Muir and Aylmore (2002);
b. Breuer and Jeffrey (2003a);
c. Lam and Dreisinger (2003);
d. Ji et al. (2003);
e. This work (Table 6.7);
f. This work.

Chu et al. (2003) noted that the decrease in thiosulfate concentration alone could not account for the decrease in the rate of gold dissolution in the presence of oxygen. The decrease in thiosulfate concentration in the first 15 minutes due to oxidation was negligible compared to the initial concentration (50 mM to 100 mM). Chu et al. (2003) suggested that the slow kinetics of gold dissolution were caused by an intermediate product ($S_2O_5^{2-}$) formed during

oxidation. However, Table 6.10 shows a significant decrease in copper(II) concentration in oxygenated ammoniacal thiosulfate solutions in the first 5-10 minutes with similar figures reported by Breuer and Jeffrey (2003a). The initial decrease in copper(II) concentration became larger at higher concentrations of oxygen or higher flow rates of air or oxygen, possibly affecting the rate of gold dissolution. It is impossible to discount either case causing the detrimental effect (copper(II) or $S_2O_5^{2-}$). As noted by Jeffrey et al. (2001a), Molleman and Dreisinger (2002), and Chu et al. (2003), this highlights the importance of an adequate control over the oxygen addition rate in order to maintain high gold dissolution. The concentration ratio of $[NH_3]$ / $[Na_2S_2O_3]$ also has a significant influence on the initial rate of gold dissolution in the presence or absence of oxygen. This can be used to propose a reaction scheme for gold oxidation as described in the following section.

Table 6.10 *Comparison of residual copper(II) concentration after aeration/oxygenation of ammoniacal-thiosulfate solutions*

$[NH_3+NH_4^+]$ (mM)	$[Na_2S_2O_3]$ (mM)	T ^oC	System	Flow rate l/min	[Cu(II)] (mM)		
					0 min	5 min	10 min
This work (pH 9.5)							
240	50	25	N_2		1.5	1.3	1.2
240	50	25	open to air		1.5	1.2	0.3
240	50	25	O_2 (0.5 mM)		1.5	0.9	0.2
Breuer and Jeffrey, 2003a							
400	100	30	O_2 (1.9 %)	1.0	10		8.6
400	100	30	air	1.0	10		5.7
400	100	30	air	0.2	10		6.6
400	100	30	air	0.1	10		7.0
400	100	30	O_2	1.0	10		6.2

6.11 Effect of concentration ratio of $[NH_3]$ / $[Na_2S_2O_3]$

6.11.1 Non-oxygenated systems

It has previously been suggested that the reaction in Eq. 6.18 is the rate determining electrochemical reaction (Jiang et al, 1993b), where $Cu(NH_3)_2^+$ is converted to more stable $Cu(S_2O_3)_3^{5-}$.

$$Au + Cu(NH_3)_4^{2+} = Au(NH_3)_2^+ + Cu(NH_3)_2^+ \quad (6.18)$$

However, the key findings in Chapter 5 and reasons given by other researchers cast doubt on this mechanism:

(i) the effect of thiosulfate on the initial rate of gold dissolution cannot be explained by Eq. 6.18 (Breuer and Jeffrey, 2000a),

(ii) gold dissolution according to Eq. 6.18 in the absence of thiosulfate was very slow at ambient temperature, while the measured potential of a gold electrode could not be correlated with the $Au(NH_3)_2^+$ species in solution due to its disproportionation (Chapter 5).

In the case of Au-Cu(II)-NH_3-$S_2O_3^{2-}$ leaching systems, ammonia and thiosulfate may be involved in the reaction of gold with thiosulfate, in the form of either free ligands or as the complexes $Cu(NH_3)_m^{2+}$, $Cu(NH_3)_p(S_2O_3)^0$ or $Au(NH_3)(S_2O_3)^-$ (m = 3 or 4, p = 2 or 3) as described by the equations in Table 5.1. For example, Wang (1992) predicted the formation of a mixed complex $Au(NH_3)(S_2O_3)^-$. The formation of this complex at a high $[NH_3]$ / $[Na_2S_2O_3]$ ratio has been supported by recent experimental results (Perera and Senanayake,

2004). Electrode potential measurements show that both $Cu(NH_3)_3^{2+}$ and $Cu(NH_3)_4^{2+}$ can exist in solution (Table 5.3), while Byerley et al. (1973b) noted the involvement of the mixed complex $Cu(NH_3)_3(S_2O_3)^0$ in thiosulfate oxidation.

The mixed complexes formed according to the general stoichiometry in Eqs. 6.19 - 6.20 can play an important role in the oxidation of both gold and thiosulfate by copper(II), depending on the nature of copper(II) species involved in each reaction and the relative concentrations of the two ligands expressed by the ratio $[NH_3] / [Na_2S_2O_3]$.

$$Cu(NH_3)_4^{2+} + S_2O_3^{2-} = Cu(NH_3)_3(S_2O_3)^0 + NH_3 \quad (6.19)$$

$$Cu(NH_3)_m^{2+} + nS_2O_3^{2-} = Cu(NH_3)_p(S_2O_3)_n^0 + (m-p)NH_3 \quad (6.20)$$

Figure 6.34 shows a reaction scheme which may be used to interpret the effect of $[NH_3]/[Na_2S_2O_3]$ on the variation of R_{Cu}, R_{Au} and R_i in oxygen free solutions; they are summarised in Figs. 6.35 – 6.38 and the conditions listed in Tables 6.11 and 6.12. An increase in the ratio of $[NH_3] / [Na_2S_2O_3]$ in copper(II) solutions without oxygen decreases the concentration of mixed copper(II)-ammonia-thiosulfate by favouring equilibrium A to the left. This lowers the rate of copper(II) reduction by thiosulfate according to reactions B1 or B2 as observed in Fig 6.35. The rate of oxidation of gold by copper(II) is also lowered due to the decrease in $Cu(NH_3)(S_2O_3)^0$, which is responsible for gold oxidation reaction (C). High thiosulfate concentration favours reaction A, and D to the right, which in turn is beneficial for thiosulfate oxidation via E and/or B1 and B2.

This is also consistent with Figs. 6.35-6.38 based on the data reported by Byerley et al. (1975), Jefrrey (2001), and from this work.

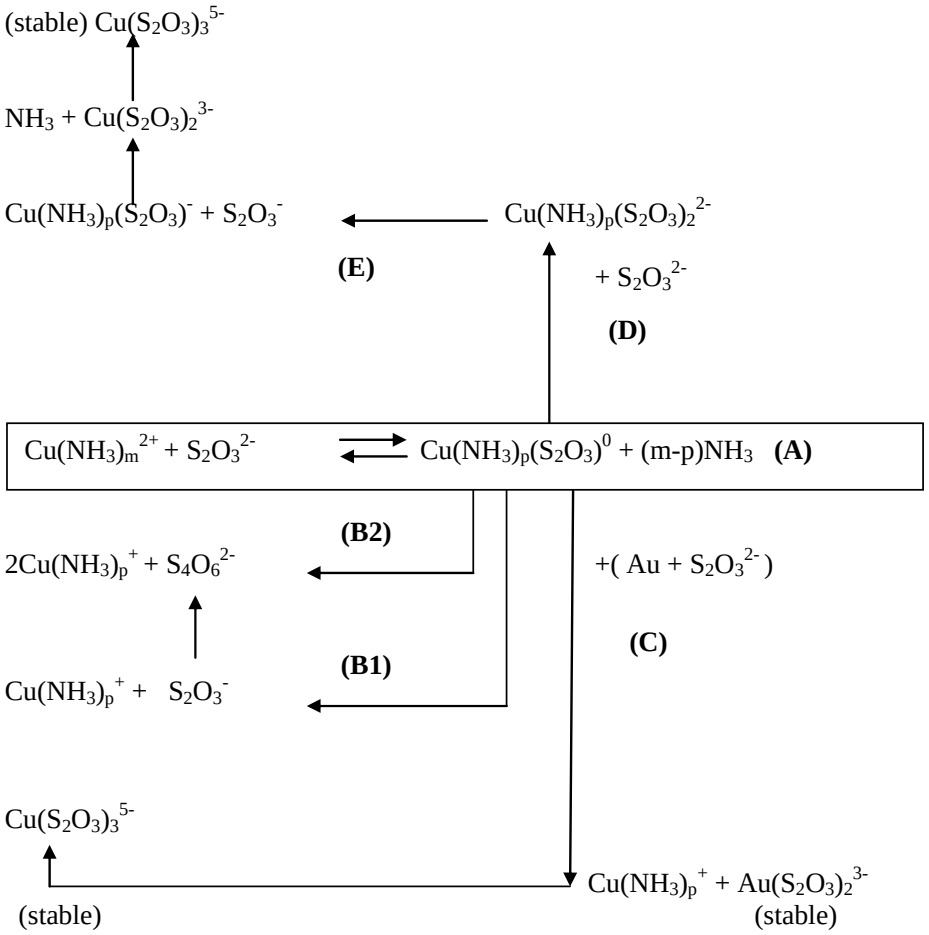


Fig. 6.34 *Proposed reaction model for the oxidation of thiosulfate and gold by copper(II) in ammoniacal solutions.*

Although the gold(I) complex $Au(S_2O_3)_2^{3-}$ formed in reaction C is stable, the copper(I) complexes formed in reactions B1, B2, C, E1 and E2 are unstable, and therefore re-equilibrate to more stable complexes such as $Cu(S_2O_3)_2^{3-}$ or $Cu(S_2O_3)_3^{5-}$. The formation of mixed copper(I) complexes such as $Cu(NH_3)_p(S_2O_3)^-$ shown in reaction E is supported by recent studies on speciation based on potentiometric studies (Black, 2006). The radical $S_2O_3^-$ dimerizes to $S_4O_6^{2-}$ (as shown in B1-B2, also happened in E) and undergoes further alkaline hydrolysis/oxidation to other products, as described in Chapter 2.

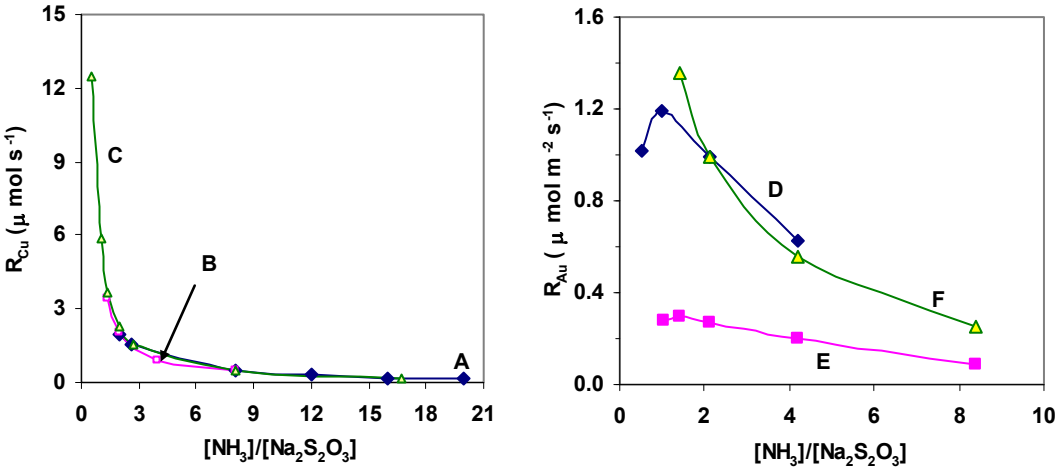


Fig. 6.35 *Effect of ammonia/thiosulfate concentration ratio on initial rate of copper(II) reduction. Data from Byerley et al. (1973b).*

Fig. 6.36 *Effect of ammonia/thiosulfate concentration ratio on initial rate of gold oxidation. Data from Jeffery (2001).*

Conditions for both figures described in Table 6.11.

Table 6.11 *Experimental conditions representing copper(II) reduction and massive gold oxidation in ammoniacal thiosulfate solutions*

Set	[Cu(II)] (mM)	$[S_2O_3^{2-}]$ (mM)	$[NH_3+NH_4^+]$ (M)	Reference
A	5	50	0.1-1.0	Byerley et al.,1973b
B	5	250 - 150	0.2	Byerley et al.,1973b
C	5	10 - 400	0.2	Byerley et al.,1973b
D	2	400	0.2-1.7	Jeffery, 2001
E	2	100 - 800	0.84	Jeffery, 2001
F	25	100 - 600	0.84	Jeffery, 2001

Temperature 30°C, literature date plotted in Figs. 6.35 - 6.38.

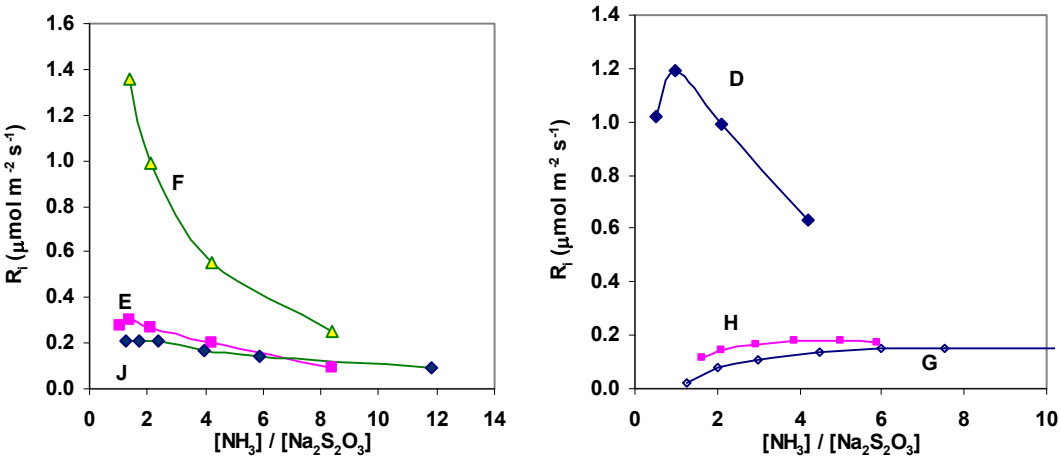


Fig. 6.37 *Effect of decreasing thiosulfate concentration on initial rate of gold oxidation. (lines E and F: data from Jeffery (2001) at 30°C).*

Fig. 6.38 *Effect of increasing ammonia concentration or pH on initial rate of gold oxidation (line D: data from Jeffery (2001) at 30°C).*
Conditions for both figures described in Tables 6.11 and 6.12.

Table 6.12 *Experimental conditions representing gold colloid oxidation in oxygenated ammoniacal thiosulfate solutions*

Set	[Cu(II)] (mM)	[O_2] (mM)	[$Na_2S_2O_3$] (mM)	[NH_4+NH_4^+] (mM)	pH
G	1.5	-	20	50-580	9.3
H	2.0	-	40	240	8.9-11
J	1.5	-	95 - 10	240	9.3
K	-	0.25	70 - 10	200	9.5
L	-	0.25	20	70 - 500	9.5
M	2.0	0.31	50 - 20	240	9.3

[Au(c)] = 0.1 mM, 25^{o}C, results plotted in Figs. 6.37-6.40.

6.11.2 Oxygenated systems

Figures 6.39 - 6.40 compare the effect of the change in [NH_3] / [$Na_2S_2O_3$] ratio on R_i in the three systems O_2-NH_3-$S_2O_3^{2-}$, N_2-Cu(II)-NH_3-$S_2O_3^{2-}$ and O_2-Cu(II)-NH_3-$S_2O_3^{2-}$. The effect of decreasing thiosulfate concentration (increasing [NH_3] / [$Na_2S_2O_3$]) appears to be different in the three cases. For example, the decrease in thiosulfate concentration had a small positive effect on R_i during oxygenation in the absence of copper(II) (curve K), but a much larger effect in the presence of copper(II) (curve M), compared to the negative effect observed under nitrogen (curve J) (Fig. 6.39). The increase in ammonia concentration showed a small negative effect on R_i in the presence of oxygen (curve L), compared to a large positive effect at low ratios of [NH_3] / [$Na_2S_2O_3$] (curves G,) in the presence of copper(II) under nitrogen (Figs. 6.38 and 6.40).

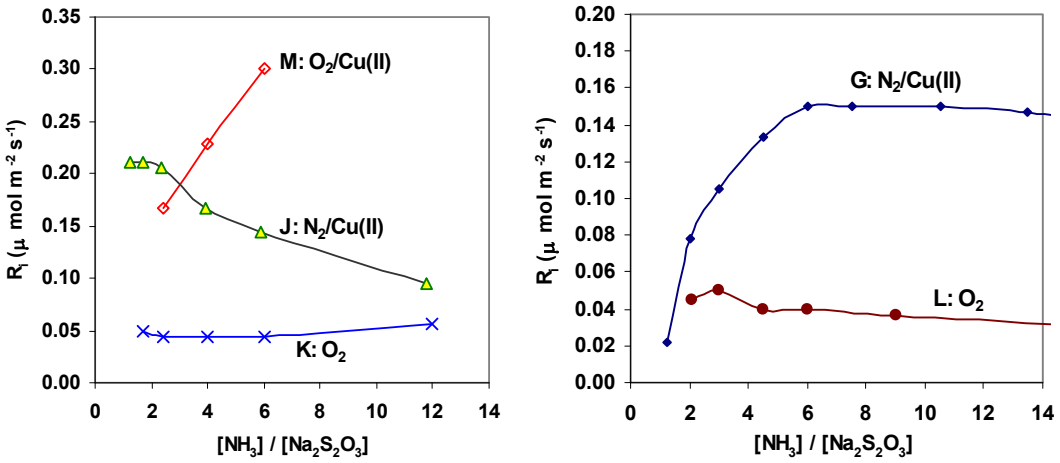


Fig. 6.39 *Effect of increasing thiosulfate concentration on initial rate of gold oxidation.*

Fig. 6.40 *Effect of increasing ammonia concentration or pH on initial rate of gold oxidation.*

Conditions for both figures described in Tables 6.11 and 6.12.

It is clear from Figs. 6.39 and 6.40 that the rate of gold dissolution is more sensitive to the ligand ratio when copper(II) is used as the oxidant, rather than oxygen. A decrease in $[NH_3]/[S_2O_3^{2-}]$ ratio favours the formation of the mixed complex $Cu(NH_3)_3S_2O_3$ according to reaction A in Fig. 6.34. Thus, the higher rates at lower ligand ratios shown in curve J of Fig. 6.39 support the view that the mixed complex is a possible oxidant for gold. A lower thiosulfate concentration (higher ratio of $[NH_3]/[S_2O_3^{2-}]$) is detrimental to gold dissolution by copper(II)/nitrogen (curve J). The opposite trend is observed in the case of copper(II)/oxygen (curve M). These results show the beneficial effect of oxygen to enhance the concentration of the actual copper(II) species responsible for gold oxidation. A further analysis of kinetics on the basis of reaction orders is described in Chapter 7.

6.12 Summary and Conclusions

The relative rates and the extent of gold dissolution at 25ºC in different lixiviant systems in a given time interval were in the order: oxygen-cyanide > copper(II)-ammonia-thiosulfate ≈ oxygen-copper(II)-ammonia-thiosulfate > oxygen-ammonia-thiosulfate ≥ oxygen-ammonia > copper (II)-ammonia.

Gold dissolution in ammoniacal copper(II) thiosulfate solutions under nitrogen had a higher activation energy (E_a = 40-50 kJ mol^{-1}) for the temperature range 22^{o}C to 48^{o}C than for that in oxygenated ammoniacal thiosulfate solutions (E_a = 25 kJ mol^{-1}) over the temperature range 25^{o}C to 48^{o}C. This suggests that the former involves a mixed chemically/diffusion controlled surface reaction, while the latter involves a diffusion controlled reaction.

The presence of silver(I) or chloride ions enhanced the rate of gold dissolution, indicating their involvement in the surface reaction.

Gold powder and unstabilized gold colloids have a higher rate of dissolution compared to gelatine stabilized colloids. This may be related to a high surface roughness factor in the case of gold powder, and without gelatine coating in the case of unstabilized colloids.

Gold dissolution in Cu(II)-NH_3-$S_2O_3^{2-}$ solution occurs through the reaction between gold, thiosulfate ions and the mixed complex $Cu(NH_3)_p(S_2O_3)^0$. Background salts, such as sulfite and carbonate decreased the concentration of

$Cu(NH_3)_p(S_2O_3)^0$ and therefore decreased the rate of gold dissolution. The negative effect of high oxygen concentration on the initial rate of gold dissolution in Cu(II)-NH_3-$S_2O_3^{2-}$ solution could be a result of the change in copper(I)/(II) speciation and/or the change in thiosulfate speciation (e.g. formation of $S_2O_5^{2-}$). Further work is essential to understand the detrimental effect of high oxygen concentration on gold dissolution.

CHAPTER 7 KINETIC MODELS FOR GOLD DISSOLUTION

7.1 Introduction

The curves representing the metal dissolution (%) as a function of time can be used to determine initial rates as well as to quantitatively analyse rate data based on kinetic models. For example, the initial rates based on differential method can be used to determine the reaction orders, which in turn can be used to propose a reaction mechanism. In general, a decrease in reaction rates of particles with time at given concentrations of reagents is a result of:

(i) the decrease in surface area which decreases the rate,

(ii) the build up of an insoluble reaction product on the particle surface which blocks the diffusion of reactants to the surface or the products away from the surface. These two situations can be quantitatively treated using a shrinking particle or shrinking core model respectively (Levenspiel, 1972). For example, McCarthy et al. (1998) showed that the unstabilized gold colloids dissolved according to a shrinking particle model.

In this chapter, the logarithmic plots of initial rates (R_i) versus concentration of reagents ([X]) are used to determine the reaction order with respect to each reagent. Electrochemical mechanism is proposed to explain the reaction orders for gold oxidation by ammoniacal copper(II) thiosulfate. The applicability of a shrinking particle model is also examined.

7.2 Reaction orders based on initial rates

The chemical reactions described in Chapter 6 explained the effect of key reagents and some of the background salts on initial rates and overall gold dissolution. As noted in Chapter 6, the initial rate of a reaction may be related to the concentration of a reactant by the Equation,

$$R_i = k\,[X]^n \qquad (7.1)$$

$$\log R_i = \log k + n \log [X] \qquad (7.2)$$

where n = reaction order with respect to [X], k = rate constant.

A double-logarithmic plot of rate against the concentration of X may give a straight line. If so, the slope is the order of the reaction with respect to reactant X. Jiang et al. (1993a) used this procedure to show that the rate of gold dissolution based on corrosion currents in solutions of 1 M sodium thiosulfate, 0.5 M ammonia, and 1 – 100 mM copper(II) maintained at pH 10 and 20 ^{o}C was first order with respect to the concentration of copper(II). Figs. 7.1- 7.5 show the log-log plots of R_i versus [X] for systems, in which the initial rates were determined at various initial concentrations of the reagent (X) in question, when all other conditions were maintained constant. Table 7.1 lists the reaction order with respect to each reagent in different lixiviant systems:

(i) effect of oxygen, sodium thiosulfate or ammonia in oxygenated (non-copper) ammoniacal-thiosulfate solutions,

(ii) effect of copper(II), sodium thiosulfate or ammonia in ammoniacal copper(II)-thiosulfate solutions,

(iii) effect of silver nitrate or sodium chloride in ammoniacal copper(II)-thiosulfate solutions,

(iv) effect of copper(II) or thiosulfate in oxygenated ammoniacal copper(II) thiosulfate solutions.

Table 7.1 *Reaction orders based on initial rate with respect to each reagent at 25°C*

[Cu(II)]* (mM)	$[O_2]^a$ (mM)	$[Na_2S_2O_3]$ (mM)	$[NH_3]_{total}$ (mM)	pH	additive	[additive] (mM)	Order
Ammoniacal copper(II)							
0.5-2.5	0	0	120	9.5	-	-	$[Cu(II)]^0$
1.5	0	0	60-240	9.3	-	-	$[NH_3]^0$
1.5	0	0	120	9.5	NaCl	0^b-330	$[NaCl]^{0.11}$
Ammoniacal copper(II) thiosulfate							
0.5-4.5	0	50	240	9.3	-	-	$[Cu(II)]^{0.41}$
1.5	0	10-95	240	9.3	-	-	$[Na_2S_2O_3]^{0.49}$
1.5	0	20	50-580	9.3	-	-	$[NH_3]^{0.60}$
2.0	0	40	240	8.9-11	-	-	$[OH]^{0.41}$
1.5	0	20	120	9.5	$NaNO_3$	50-330	$[NaNO_3]^0$
					NaCl	0^b-330	$[NaCl]^{0.15}$
					$AgNO_3$	0.01-0.15	$[AgNO_3]^{0.20}$
					Ag(c)	0.05-0.1	$[Ag(c)]^0$
Oxygenated thiosulfate							
0	0.25	10-70	0 (I = 0.21)	9.3	-	-	$[Na_2S_2O_3]^0$
0	0.25	30	0	9.5	NaCl	50-330	$[NaCl]^0$
0	0.25-0.75	50	0 (I = 0.21)	9.3		-	$[O_2]^0$
Oxygenated ammonia							
0	0.25	0 (I = 0.21)	67-280	9.5	-	-	$[NH_3]^{0.33}$
0	0.25	0	120	9.5	NaCl	50-330	$[NaCl]^0$
Oxygenated ammoniacal thiosulfate							
0	0.25	20	67-500	9.5	-	-	$[NH_3]^0$
0	0.25	10-70	200	9.5	-	-	$[Na_2S_2O_3]^0$
0	0.06-0.75	50	240	9.3	-	-	$[O_2]^{0.28}$
0	0.25	20	120	9.5	NaCl	50-330	$[NaCl]^0$
Oxygenated ammoniacal copper(II) thiosulfate							
1.0-3.0	0.31	50	240	9.3	-	-	$[Cu(II)]^{0.98}$
2.0	0.31	20-50	240	9.3	-	-	$[Na_2S_2O_3]^{-0.64}$

a. Zero oxygen indicates nitrogen atmosphere.*Initial copper(II) concentration.

b. At [NaCl] = 0 mM, the solution of colloidal gold prepared using $NaAuCl_4$, which contains 0.4 mM Cl^-.

In oxygenated ammoniacal-thiosulfate solutions without copper(II), the concentration of oxygen affected the reaction rates, showing a reaction order of 0.28 (Fig. 7.1). The change in concentration of ammonia, thiosulfate and chloride appeared to have no affect on reaction rates (appendix A4.1a, A4.1c; A4.2c; A4.3a). However, in the absence of thiosulfate, the rate of gold dissolution had a reaction order of 0.32 with respect to ammonia (Fig. 7.1).

In ammoniacal copper(II)-thiosulfate solutions without oxygen, the concentrations of copper(II), ammonia, and thiosulfate appeared to affect the reaction rates, with reaction orders 0.41, 0.49 and 0.60 respectively. However, at higher concentrations the reaction order was zero order with respect to ammonia and thiosulfate (B, C in Fig. 7.2).

The reaction order with respect to silver(I) in the presence of thiosulfate was 0.2, and that with respect to chloride in the presence or absence of thiosulfate was about 0.1-0.15. Since the colloidal gold solution was prepared using $NaAuCl_4$, a solution of 0.1 mM gold colloid would contain 0.4 mM Cl^-. Thus, the measured value of R_i at [NaCl] = 0 mM corresponds to $[Cl^-]$ = 0.4 mM (log $[Cl^-]$ = -3.4). The fact that this point fits with the other data points to give a good linear relationship (Fig. 7.3) is consistent with the catalytic role of chloride on gold oxidation by ammoniacal copper(II) thiosulfate proposed in Chapter 6.

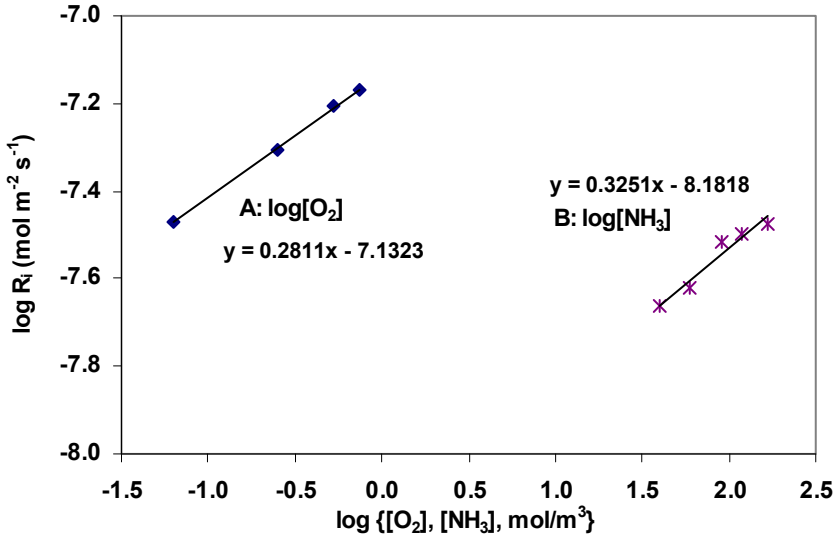


Fig. 7.1 *Logarithmic plot of initial rate of gold oxidation as a function of oxygen or ammonia concentration in non-copper solutions.*

A: [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3.

B: [O_2] = 0.25 mM, [$Na_2S_2O_3$] = 0 mM, pH = 9.5.

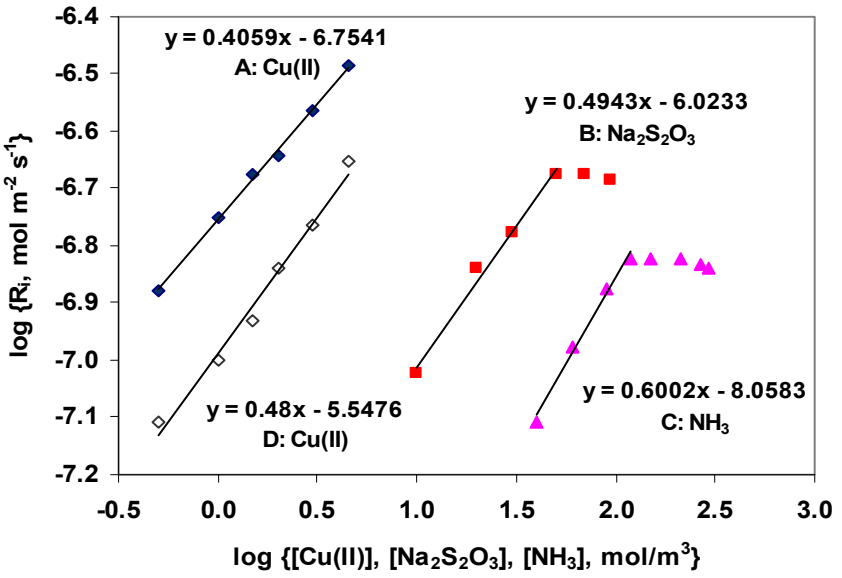


Fig. 7.2 *Logarithmic plot of initial rate of gold oxidation by copper(II) as a function of reagent concentration in anaerobic solutions.*

(60 minutes initial reaction period was taken for line D).

A: [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3.
B: [Cu(II)] = 1.5 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3.
C: [Cu(II)] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, pH = 9.3.
D: [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

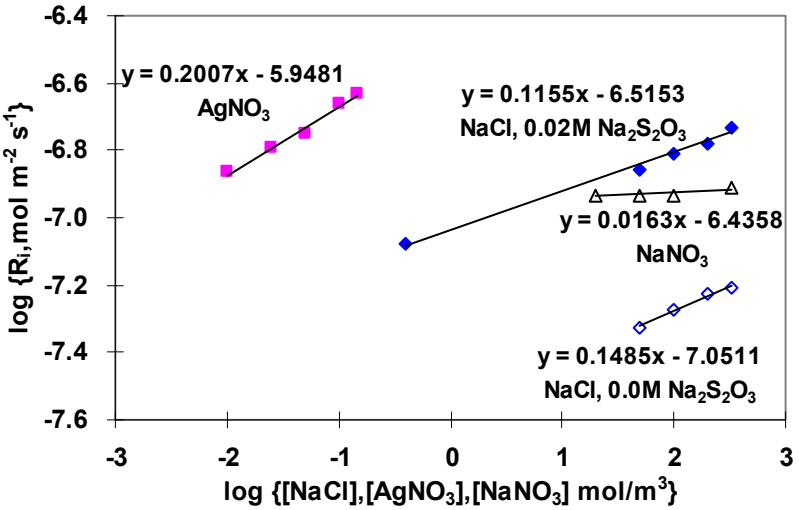


Fig. 7.3 *Logarithmic plot of initial rate of gold oxidation as a function of chloride, nitrate, or silver(I) concentration in anaerobic solutions. [$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.*

Figure 7.4 shows a logarithmic plot of R_i versus initial [Cu(II)] based on the data in Table 7.2, and compares the effect of initial copper(II) concentration on the initial rate of dissolution of gold colloids and powder. The reaction order is close to 0.5 in both cases with respect to the initial copper(II) concentration. This behaviour is different from the results reported by Jiang et al. (1993a) and Jeffrey (2001) which showed a first order reaction with respect to copper(II) concentration at low concentration. For example, the rates based on gold-silver alloy (5%Ag) reported by Jeffrey (2001) plotted in Fig. 7.4 show higher rates and a slope close to 1.

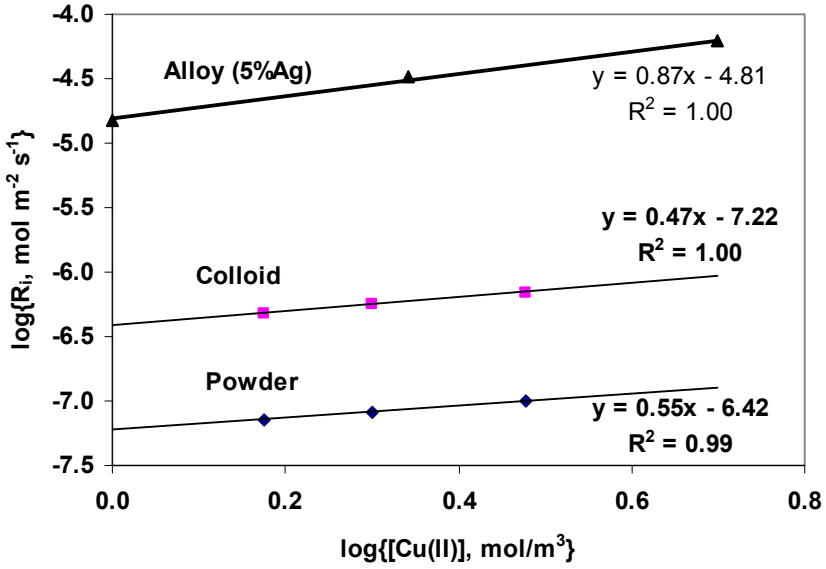


Fig. 7.4 *Logarithmic plot of initial rate of gold oxidation as a function of copper(II) concentration in anaerobic solutions.*
[Au] (powder or colloid) = 0.1 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5. Data for gold-silver alloy (5%) are based on REQCM (Jeffrey, 2001) at 0.84 M total ammonia, and 0.4 M sodium thiosulfate at 30 °C.

Table 7.2 *Effect of copper(II) on initial rate of gold colloid and powder oxidation*

[Cu(II)] (mM)	R_i (μM /min.) *		R_i (μmol m^{-2} s^{-1})		Gold dissolution (%) in 1 hr.	
	Colloid	Powder	Colloid	Powder	Colloid	Powder
1.5	1.3	0.075	0.072	0.47	40	6
2.0	1.5	0.091	0.083	0.57	45	7
3.0	1.8	0.111	0.10	0.69	57	9

[$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5. [Au(c)] = 0.1 mM, [Au(s)] = 0.1 mM.

* 60 minutes initial reaction period was taken.

In oxygenated ammoniacal copper(II) thiosulfate solutions, the effect of copper(II) and thiosulfate concentrations on reaction rate showed a reaction order of 0.98 and -0.64 respectively, compared with 0.41 and 0.49 in the absence of oxygen (Fig.7.5). This indicates the complex role of oxygen in the reaction scheme responsible for gold oxidation by copper(II).

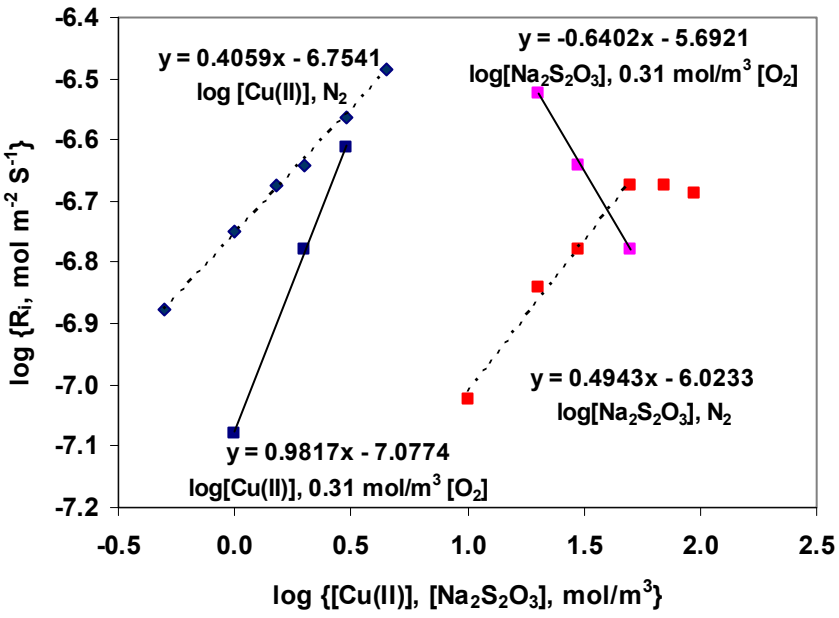


Fig. 7.5 *Logarithmic plot of initial rate of gold oxidation as a function of copper(II) and thiosulfate concentration in oxygenated or anaerobic solutions.*

7.3 Rate controlling step for the dissolution of gold by copper(II) in oxygenated solution

In Chapter 6, it was shown that the first order dependence of rate of dissolution of gold-silver alloy on copper(II) concentration at low concentrations based on REQCM studies (Jeffrey, 2001) was a result of the diffusion (mass transport) controlled reaction described by the Levich equation (Fig. 6.9). Thus, the first order dependence of the rate of dissolution of gold colloid in oxygenated copper(II)-ammonia-thiosulfate solutions shown in Fig. 7.5 is also likely to be a result of the mass transfer controlled nature of the surface reaction. The y-intercept of the linear relationship in Fig. 7.5 (logk = -7.1) corresponds to k = 8 x 10^{-8} m s^{-1}.

This value can be compared with the calculated convective mass transfer coefficient for suspended particles based on the following equations (Cussler, 1997).

$$k_m = \frac{ShD}{L} \tag{7.3}$$

$$Sh = 2 + 0.6Gr^{1/4}Sc^{1/3} \tag{7.4}$$

$$Gr = \frac{L^3 g(\Delta\rho / \rho)}{\nu^2} \tag{7.5}$$

$$Sc = \frac{\nu}{D} \tag{7.6}$$

The dimensionless terms in Eqs. 7.3 - 7.6 are: Sh = Sherwood number, Gr = Grashof number, Sc = Schmidt number, and Δρ/ρ = fractional density change. Other terms are: D = diffusion coefficient, L = characteristic length (particle diameter), and v = kinematic viscosity.

Table 7.3 lists the values of the dimensionless numbers and the resultant value of k_m = 0.5 m s^{-1} for the mass transfer coefficient of copper(II). This value is six orders of magnitude larger than the value of k = 8 x 10^{-8} based on experimental values shown in Fig. 7.5. These results highlight the importance of considering a surface reaction mechanism to rationalise the rate controlling chemical reaction for colloidal gold instead of mass transfer of reagents to the surface.

Table 7.3 *Calculation of mass transfer coefficient of copper(II) to gold surface*

Property	Symbol	Value
Characteristic length (particle diameter)	L	20 x 10^{-9} m
Diffusion coefficient	D	4.6 x 10^{-9} m^2 s^{-1} (a)
Kinematic viscosity	v	8.9 x 10^{-7} m^2 s^{-1} (a)
Acceleration due to gravity	g	9.8 m s^{-2}
Fractional density change	$\Delta\rho/\rho$	0.95 (b)
Grashof number	Gr	9.4 x 10^{-11}
Schmidt number	Sc	1.9 x 10^2
Sherwood number	Sh	2.0
Mass transfer coefficient	k_m	0.46 m s^{-1}

(a) Jeffrey (2001).

(b) $\Delta\rho/\rho = (\rho_{gold} - \rho_{water})/ \rho_{gold}$.

Reactions in Eqs. 7.8 - 7.9 may be written instead of Eq. 7.7 reported in previous studies (Jiang et al., 1993b). The participation of chloride ion considered in Eq. 7.8 accommodates the catalytic effect of chloride ions noted in Fig. 7.3. The unstable gold(I) species: $Au(NH_3)Cl^0$ and $Au(NH_3)(S_2O_3)^-$ formed in Eqs. 7.8 - 7.9 will rapidly react with thiosulfate ions to produce more stable $Au(S_2O_3)_2^{3-}$ ions, while copper(I) ions will be re-oxidized to copper(II).

$$Au + Cu(NH_3)_4^{2+} = Au(NH_3)_2^{+} + Cu(NH_3)_2^{+} \quad (7.7)$$

$$Au + Cu(NH_3)_pCl^{+} = Au(NH_3)Cl^{0} + Cu(NH_3)_{p-1}^{+} \quad (7.8)$$

$$Au + Cu(NH_3)_p(S_2O_3)^{0} = Au(NH_3)(S_2O_3)^{-} + Cu(NH_3)_{p-1}^{+} \quad (7.9)$$

In recent studies Wensveen and Nicol (2005) confirmed the formation of an intermediate mixed ammine/thiosulfate copper(II) complex ion and considered the equilibrium between $Cu(NH_3)_4(H_2O)_2^{2+}$, $Cu(NH_3)_4(H_2O)(S_2O_3)^0$, $Cu(NH_3)_4(H_2O)(Cl)^+$, and $Cu(NH_3)_4(H_2O)(SO_4)^0$ described in Fig. 7.6. They also found that:

(i) the reduction of copper(II) and the accompanying oxidation of thiosulfate in the absence of oxygen occurs by way of the mixed complex $Cu(NH_3)_4(H_2O)(S_2O_3)^0$,

(ii) in the presence of dissolved oxygen, the copper(I) thiosulfate complexes are only very slowly oxidised by oxygen, while copper(I) diammine complex is rapidly oxidised to copper(II) state,

(iii) at low ratios of $[NH_3]/[S_2O_3^{2-}]$, the rate of reduction of copper(II) is rapid, but an apparent steady state is achieved in which the concentration of $Cu(NH_3)_4(H_2O)(S_2O_3)^0$ remains relatively constant, while oxygen continues to be consumed in the oxidation of thiosulfate,

(iv) at higher ratios of $[NH_3]/[S_2O_3^{2-}]$ the steady state concentration of $Cu(NH_3)_4(H_2O)(S_2O_3)^0$ is higher.

Thus, the increase in initial rate of gold dissolution by copper(II) with the increase in $[NH_3]/[S_2O_3^{2-}]$ in oxygenated solutions shown in Fig. 6.39, which appears to be first order with respect to total copper(II) concentration in Fig. 7.5,

is in favour of the involvement of $Cu(NH_3)_p(S_2O_3)^0$ in the rate controlling step for gold dissolution (Eq. 7.9).

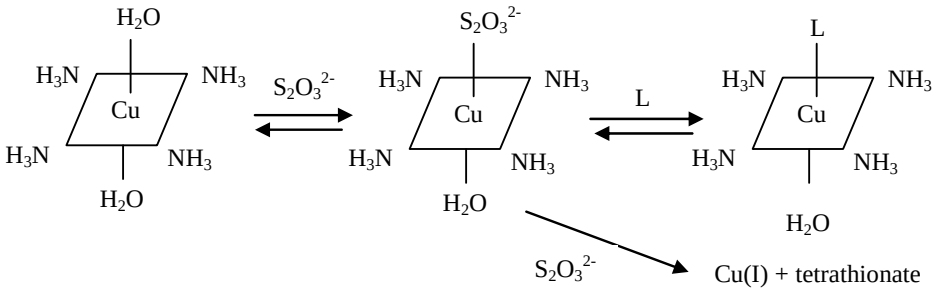


Fig. 7.6 *Reaction equilibria involved in the oxidation of thiosulfate by copper(II). The competing ligand L can be NH_3, SO_4^{2-}, Cl^-. (Wensveen and Nicol, 2005).*

Fig. 7.5 shows a decrease in the initial rate of gold oxidation by copper(II) at higher concentrations of thiosulfate in oxygenated solutions, leading to a reaction order of -0.64. This may be related to a decrease in the concentration of copper(II) species $Cu(NH_3)_p(S_2O_3)^0$, which is responsible for gold leaching, as a result of the formation of $Cu(NH_3)_p(S_2O_3)_2^{2-}$ leading to reaction E (reactions D and E in Fig. 6.34).

Table 7.4 lists the rate of gold dissolution based on gold foils (Feng and van Deventer, 2007b) and gold colloids to show the detrimental effect of excess oxygen. For example, an increase in oxygen concentration from 0.25 mM to 0.63 mM decreased the rate of dissolution of colloidal gold by ~50% at low reagent concentrations of 1.5 mM copper(II), 50 mM sodium thiosulfate and 240 mM ammonia. Feng and van Deventer (2007b) used a more concentrated system with respect to all three reagents: 6 mM copper(II), 500 mM ammonia, and 100 mM thiosulfate, and the rate decreased by ~50% when the solution

was open to air instead of nitrogen. This means that the detrimental effect of oxygen is greater at higher reagent concentrations.

Table 7.4 *Comparison of initial rates of gold dissolution at 25 ^{o}C.*

$[O_2]$ (mM)	[Cu(II)] (mM)	$[Na_2S_2O_3]$ (mM)	$[NH_3+NH_4^+]$ (mM)	pH	10^7 R (mol m^{-2} s^{-1})
Colloidal gold (this work)					
0 0.25-0.06[a,b] 0.50 0.63	1.5	50	240	9.5	2.0 2.0 1.7 1.1
Gold foil (Feng and van Deventer, 2007b)					
0 Air[a]	6	100	500		62 27

a. open to air.
b. O_2 concentration decreased from 0.25 mM to 0.06 mM in 15 minutes.

Wensveen and Nicol (2005) noted that at higher thiosulfate concentrations, oxygen consumption by thiosulfate continued well after the steady state had been reached. Byerley et al. (1975) proposed a mechanism that involved thiosulfate degradation via $Cu(II)(NH_3)_p$-$S_2O_3^{2-}$-O_2 and $S_2O_5^{2-}$, which is supported by the lower gold recovery in the leaching of gold powder at increased flow rates of air/oxygen, or in the presence of $Na_2S_2O_5$ (Jeffrey et al., 2003). Feng and van Deventer (2007b) also found that the extent of dissolution of pure gold decreased in the presence of oxygen, where air or oxygen bubbling caused a higher consumption of thiosulfate and passivation of gold. Further studies and discussion on these aspects in oxygenated systems are beyond the scope of this thesis. However, it is important to consider the possible reasons for different reaction orders with respect to different reagents listed in Table 7.1 in the absence of oxygen.

7.4 Electrochemical model for the dissolution of gold by copper(II) in anaerobic solutions

It was shown in Chapter 6 that the first order dependence of the rate of dissolution of gold-silver (5%Ag) alloy in ammoniacal copper(II) thiosulfate solutions was a result of the diffusion controlled nature of the reaction, where the mass transport of copper(II) to the gold surface was rate controlling. Jiang et al. (1993a) reported the rate of gold dissolution based on the corrosion currents measured in a solution of 1 M thiosulfate of pH 10, which contained different concentrations of $Cu(NH_3)_4^{2+}$ in the range 1 - 100 mM at 20 ^oC. Their results and the relevant rates are listed in Table 7.5. A logarithmic plot of R_{corr} versus [Cu(II)] gave a straight line to which the equation $\log R_{corr} = 0.97 \log[Cu(II)] - 6.25$ can be fitted. The value of the rate constant based on the y-intercept is $k_1 = 10^{-6.25} = 6.6 \times 10^{-7}$ mol m^{-2} s^{-1}. This value is 6.6 times larger than the value of $k_1 = 8.5 \times 10^{-8}$ for gold colloids based on Fig. 7.5. This may be related to impurities such as silver or the higher surface roughness factor associated with the massive gold compared to colloidal gold.

Table 7.5 *Effect of $Cu(NH_3)_4^{2+}$ concentration on the dissolution rate of gold*

$Cu(NH_3)_4^{2+}$ / (mM)	1	10	50	100
i_{corr} / μA $cm^{-2(a)}$	5.62	50.1	194	573
10^7 R_{corr} / mol m^{-2} s^{-1}	5.80	51.9	201	595

(a). Corrosion currents at mixed potentials; 1 M thiosulfate, pH 10, 20°C;
(i_{corr} from Jiang et al.(1993a); R_{corr} = i_{corr}/nF: n = 1, F = 96487 C mol^{-1}).

In contrast, the mass transfer coefficient to colloidal gold particles is much larger (k_m = 0.46 m s^{-1}) than the measured rate constant (k = 8 x 10^{-8} m s^{-1}) based on the first order dependence of rate with respect to the concentration of copper(II) in oxygenated solutions. Electrochemical models can be considered to explain the half order reactions with respect to oxidant and ligand concentration based on initial rates under anaerobic conditions (N_2 atmosphere). Heterogeneous kinetic models such as the shrinking sphere or shrinking core models are more useful for the quantitative analysis of gold dissolution curves. Further analysis of these results on the basis of proposed reaction mechanism(s) follow.

A half order reaction with respect to the concentration of a ligand or oxidant is an indication of simultaneous anodic and cathodic reaction at the same rate, as described by the corrosion theory (Pesic and Sergent, 1993; Nicol and Lazaro, 2002). Eqs. 7.10 - 7.12 show possible half-cell reactions with different ligands involved in the anodic reaction. The actual coordination sphere of copper(II) involves one or more of the four ligands: NH_3, $S_2O_3^{2-}$, OH^- and Cl^-, as well as other associated anions SO_4^{2-}, $S_4O_6^{2-}$, and CO_3^{2-}. For simplicity copper(II) is shown by Cu(II) in Eq. 7.13.

Anodic half reaction with ligand X (X = $S_2O_3^{2-}$, NH_3 or Cl^-)

$$Au(c) + X^{n-} = Au(X)^{n-} (ads) \quad (7.10)$$

$$Au(X)^{n-} (ads) = Au(X)^{-(n-1)} (ads) + e^- \text{ (rate controlling)} \quad (7.11)$$

$$Au(X)^{-(n-1)} (ads) + X^{n-} = Au(X)_2^{-(2n-1)}(aq) \quad (7.12)$$

Cathodic half reaction

$$Cu(II) + e^- = Cu(I) \text{ (rate controlling)} \quad (7.13)$$

According to the electrochemical model the oxidation and reduction half cell reactions occur at the same rate at the mixed potential, leading to the rate equations described by the following expression:

$$R_i = k[Cu(II)]^{0.5}[X]^{0.5} \quad (7.14)$$

Equation 7.14 may explain the reaction orders close to 0.5 with respect to $S_2O_3^{2-}$, NH_3, and Cu(II) (Table 7.1) for the oxidation of gold by copper(II). In order to verify Eq. 7.14, Fig. 7.7 plots the rate as a function of $\{[Cu(II)][X]\}^{0.5}$ for different initial concentrations of copper(II), while the concentration of ligands, X = $S_2O_3^{2-}$ or NH_3, remained constant. The slopes of the linear relationships correspond to a rate constant of k = 2 x 10^{-8} m s^{-1} (X = $S_2O_3^{2-}$) and k = 1 x 10^{-8} m s^{-1} (X = NH_3). Figs. 7.8 and 7.9 show similar plots and slopes based on the results obtained in experiments conducted using solutions of constant initial copper(II) concentration, but varying concentrations of thiosulfate (Fig. 7.8) or ammonia (Fig. 7.9). The rate constants (1 x 10^{-8} – 2 x 10^{-8} m s^{-1}) in anaerobic

ammoniacal copper(II) thiosulfate solutions based on Figs. 7.7 - 7.9 are less than $k = 8 \times 10^{-8}$ m s^{-1} determined in oxygenated ammoniacal copper(II) thiosulfate solutions. However, the three values are of the same order 10^{-8} m s^{-1}. A plot of R_i as a function of $[Cu(II)]^{0.5}[X]^{0.5}$ is expected to give a straight line of slope k, which passes through the origin according to Eq. 7.14. Fig. 7.7 shows an intercept of 3×10^{-8} m s^{-1} for both linear relationships. This means that there is another reaction which is responsible for gold dissolution.

Further analysis of rate requires exact concentrations of the actual copper(II) species, free thiosulfate ion and ammonia concentrations which are dependent on the ionic strength and the association (ion-pairing) constants (Black, 2006). Such analysis is beyond the scope of this investigation due to the lack of thermodynamic data.

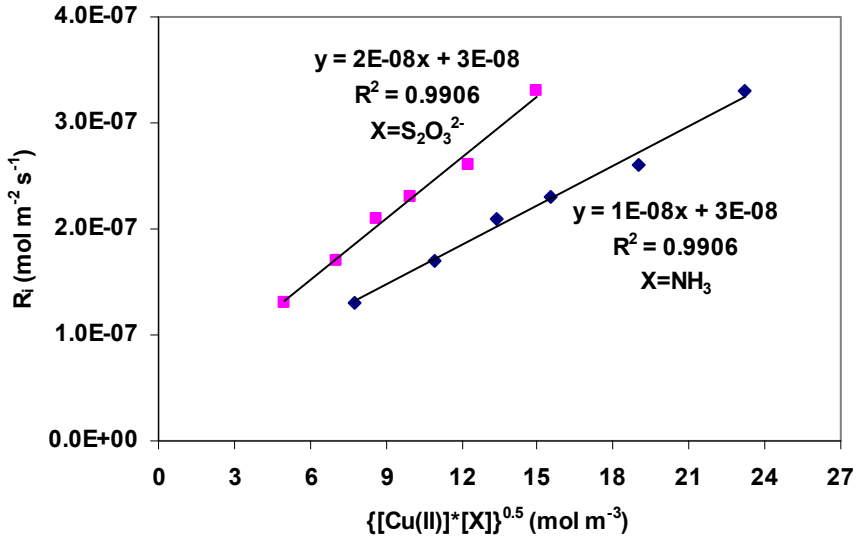


Fig. 7.7 *Initial rate of gold oxidation as a function of {[Cu(II)]*[X]}$^{0.5}$ at variable copper(II) concentrations in ammonia-thiosulfate solutions under nitrogen.*

[Au(c)] = 0.1 mM, [Cu(II)] = 0.5-4.5mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3, 25^oC

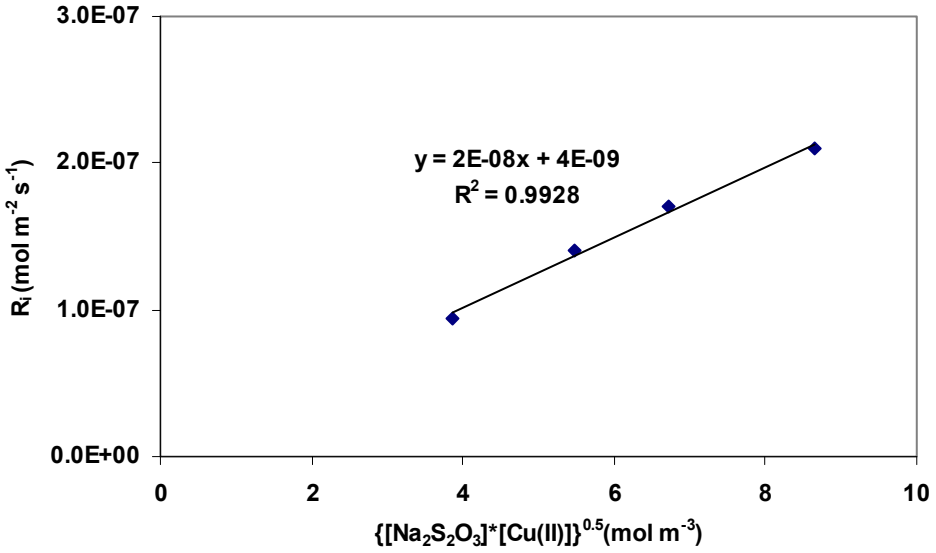


Fig. 7.8 *Initial rate of gold dissolution as a function of {[Cu(II)]*[$S_2O_3^{2-}$]}$^{0.5}$ at variable thiosulfate concentrations in copper(II)-ammonia solutions under nitrogen.*

[Au(c) = 0.1 mM, [Cu(II)]= 1.5mM, [$Na_2S_2O_3$] = 10-50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3, 25^oC.

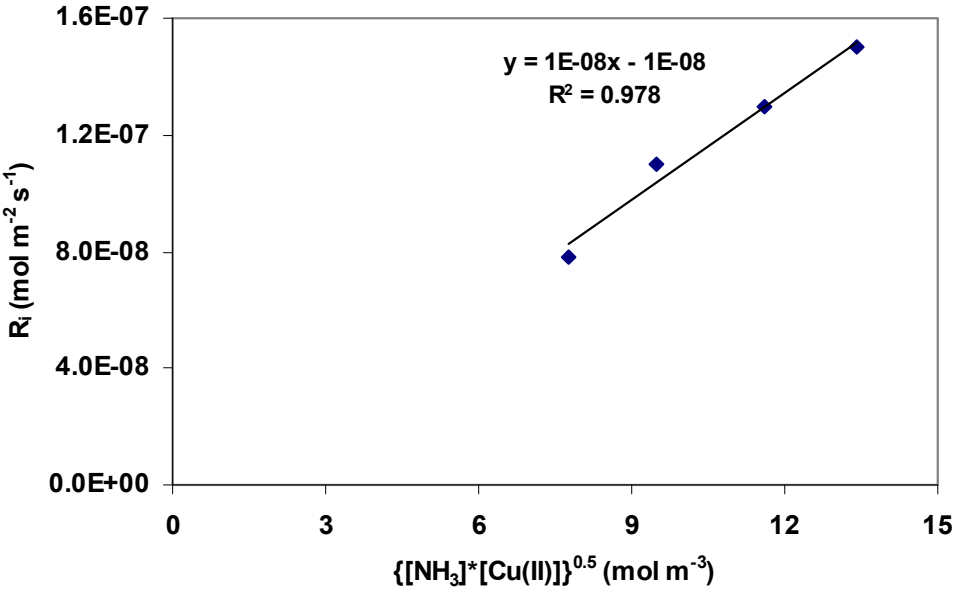


Fig. 7.9 *Initial rate of gold oxidation as a function of* $\{[Cu(II)]^*[NH_3]\}^{0.5}$ *at variable ammonia concentrations in copper(II)-ammonia solution under nitrogen.* $[Au(c)] = 0.1$ *mM,* $[Cu(II)] = 1.5$*mM,* $[Na_2S_2O_3] = 20$ *mM,* $[NH_3+NH_4^+] = 80$*-240 mM, pH = 9.3, 25*^oC.

7.5 Shrinking particle kinetic models

The decrease in the slope of the dissolution curves in Figs. 6.1 - 6.3 can be attributed to one of three factors:

(i) the decrease in the remaining gold colloid and hence the total gold surface area available for reaction, or

(ii) the increase in the thickness of an insoluble surface layer which retards the diffusion of:

(a) reactants to the reaction sites, or

(b) products into the bulk solution.

(iii) the decrease in concentration(s) of reagent(s) involved in the surface reaction.

The shrinking sphere and shrinking core kinetic models (Levenspiel, 1972) describe the first two situations, as expressed by Eqs. 7.15 and 7.16 respectively:

$$1-(1-X)^{1/3}=\left(\frac{bkC}{r\rho}\right)t=k_{ss}t \qquad (7.15)$$

$$1-3(1-X)^{2/3}+2(1-X)=\left(\frac{6DC}{r^2\rho}\right)t=k_{sc}t \qquad (7.16)$$

for the reaction: A(aq) + bB(s) → product.

where X is the fraction of gold colloid dissolved at time t, k_{ss} and k_{sc} are the respective apparent rate constants for the shrinking sphere and shrinking core models, C is the concentration of the reactant, D is the diffusion coefficient, r is the initial particle radius, and ρ is the molar density of gold, k is the intrinsic rate constant.

McCarthy et al. (1998) showed the validity of a shrinking sphere model for the cyanidation of gold colloids of particle size 15 nm in aerated 28 mM sodium cyanide solutions at 20^{o}C. While the electron-microscope studies suggested the dissolution of colloidal particles in a uniform shrinking particle manner, a plot of $1-(1-X)^{1/3}$ as a function of time (t) showed a linear relationship of slope k_{ss} = 2 x 10^{-3} s^{-1} based on the results obtained using cyanide solutions containing 0.042 mM colloids. Calculations based on film diffusion showed that the mass transfer coefficient of oxygen to the colloid surface was 0.1 m s^{-1} compared to the value of k = 1 x 10^{-6} m s^{-1} based on Eq. 7.15. Thus, the rate of

cyanidation of gold colloids in aerated solutions is lower than the rate of mass transport of oxygen to the gold surface (McCarthy et al., 1998). Due to the high mass transfer coefficient of oxygen compared to the intrinsic rate constant k for the surface reaction, the rate of cyanidation of colloidal gold is independent of dissolved oxygen concentration. This has been observed by McCarthy et al. (1998) and Hindmarsh and Nicol, (2001).

Likewise, the mass transfer coefficient of copper(II) ions to the colloidal gold surface (0.46 m s^{-1}, Table 7.3) is larger than the rate constant of the surface chemical reaction (≈10^{-8} m s^{-1}) based on the slopes of the linear relationships in Figs. 7.5, 7.7, 7.8, and 7.9. Thus, it is possible to examine the applicability of the shrinking sphere/core models to the dissolution of colloidal gold in ammoniacal copper(II) thiosulfate solutions. However, the applicability of these models depends on whether the term C in Eqs. 7.15 - 7.16 is unchanged during the reaction period under consideration. This is questionable, especially in the case of gold oxidation by copper(II), where the concentration of residual copper(II) varies with time, depending on the composition and the availability of oxygen. However, in oxygenated copper(II)-ammonia-thiosulfate solutions of low ratios $[NH_3]/[S_2O_3^{2-}]$, an apparent steady state is achieved in which the concentration of $Cu(NH_3)_4(H_2O)(S_2O_3)^0$ remains relatively constant while oxygen is continually consumed in the oxidation of thiosulfate (Wensveen and Nicol, 2005). Thus, the applicability and limitations of a shrinking particle model for the thiosulfate leaching of gold with respect to the rate controlling surface reaction are discussed in the following sections.

7.6 Shrinking sphere model in copper(II)-ammonia-thiosulfate media

7.6.1 Conditions and limitations

At a higher concentration of copper(II) (1.5 mM) and low concentrations of thiosulfate (20 mM) and ammonia (120 mM), the rate data can be described by a shrinking sphere model as shown in Figs. 7.10 and 7.11 for colloidal gold and gold powder respectively. A plot of $1-(1-X)^{1/3}$ versus t gives a straight line in both figures. Likewise, Fig. 7.12 shows that the shrinking sphere model is the best fit at low ammonia concentrations. Liddell (2005) noted the limitations of both shrinking sphere and core models when the values of X cover a limited range ($0 \leq X \leq 0.1$) indicating a low fraction reacted, such as in Fig. 7.11, causing uncertainty in both models. The applicability of these models for results obtained in solutions of high ammonia also remains uncertain, neither shrinking sphere nor shrinking core models fit the data in Fig. 7.13. In addition, the change in copper(II) concentrations during reaction with thiosulfate could also affect the analysis of the experimental data over 2 - 3 hours. The validity of the shrinking sphere model can be further examined by considering the effect of particle radius and reagent concentration on the apparent rate constant.

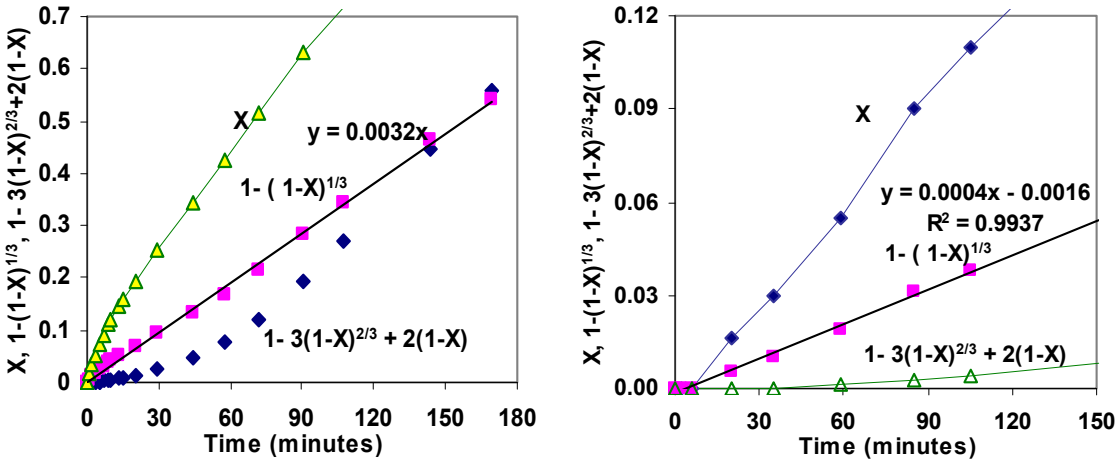


Fig. 7.10 *Validity of shrinking sphere model for gold colloids in copper(II)-ammonia-thiosulfate solutions under nitrogen.*

Fig. 7.11 *Validity of shrinking sphere model for gold powder in copper(II)-ammonia-thiosulfate solutions under nitrogen.*
For both figures: [Cu(II)] = 1.5 mM, [NH_3+NH_4^+] = 120 mM, [$Na_2S_2O_3$] = 20 mM, pH 9.5 at 25˚C.

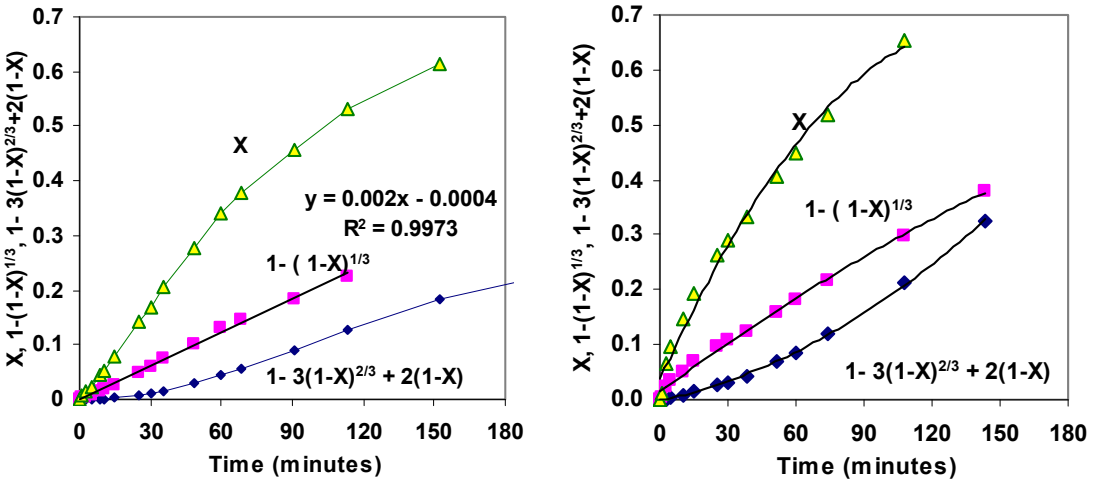


Fig. 7.12 *Validity of shrinking sphere/core model for gold colloid in copper-ammonia (low)-thiosulfate solutions under nitrogen.*

Fig. 7.13 *Validity of shrinking sphere/core model for gold colloid in copper(II)-ammonia (high)-thiosulfate solutions under nitrogen.*
[Cu(II)] = 1.5 mM, [NH_3+NH_4^+] = 50 mM (left) or 300 mM (right), [$Na_2S_2O_3$] = 20 mM, pH 9.3 at 25˚C.

7.6.2 Effect of particle size and copper(II) concentration

Figures. 7.14 - 7.15 show the plots based on a shrinking sphere kinetic model for the dissolution of gold colloids of different particle sizes under the same experimental conditions. The validity of a shrinking sphere model can be tested using Eq. 7.17, which indicates that a logarithmic plot of k_{ss} versus bC/ρr should be a straight line of slope ~1. Fig. 7.16 shows a good linear relationship with a slope of ~1, with or without the data point corresponding to unstable gold colloids, and a y-intercept of log k = -7.3. This indicates that the reaction rate is controlled by the surface reaction and that the intrinsic rate constant is $k = 10^{-7.3} = 0.5 \times 10^{-7}$ m s^{-1}.

$$\log(k_{ss}) = \log\left(\frac{bC}{r\rho}\right) + \log k \qquad (7.17)$$

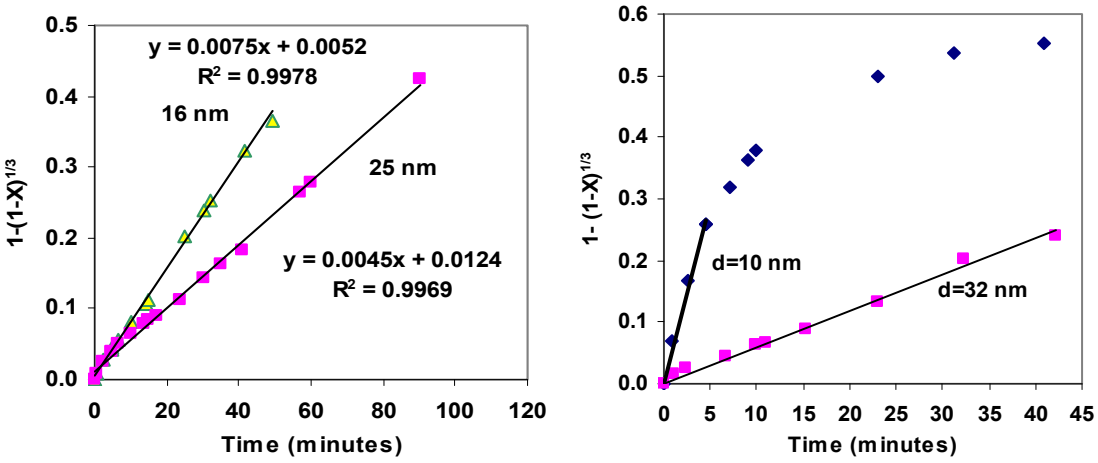


Fig. 7.14 *Shrinking sphere model for the dissolution of stabilized gold colloids of different particle size in copper(II)-ammonia-thiosulfate solutions under nitrogen.*

Fig. 7.15 *Shrinking sphere model for the dissolution of unstabilized gold colloids in copper(II)-ammonia-thiosulfate solutions under nitrogen.*
[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

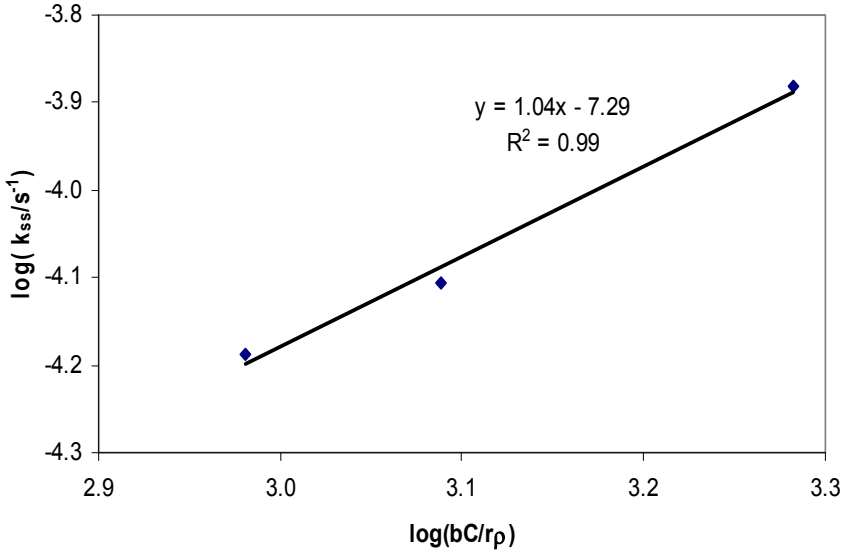


Fig. 7.16 *Logarithmic plot of k_{ss} as a function of (bC/rp) for colloidal gold of different particle size (data from Figs. 7.14-7.15, particles sizes are 16nm, 25nm and 32nm, they are all fit to shrinking sphere model over 40 minutes).*

Figures 7.17 and 7.18 show the applicability of the shrinking sphere model for the dissolution of gold powders and examine the effect of particle size (Fig. 7.17) and the initial copper(II) concentration (Fig. 7.18). The values of k_{ss} from the slopes of the linear relationships in Figs. 7.17 - 7.18 can be used in Eq. 7.18, along with b =1, ρ = 97970 mol m^{-3}, and the values of r and C, to calculate a value for k in each case. The calculated values of k = 3.2 x 10^{-7}- 9 x 10^{-7} m s^{-1} listed in Table 7.6 for gold powders are an order of magnitude larger than the value of k = 0.5 x 10^{-7} m s^{-1} for gold colloids based on Fig. 7.16. Again, this may be related to the larger surface roughness factor of the particles of gold powder compared to gold colloids.

$$\log k = \log(k_{ss} r\rho / bC) \qquad (7.18)$$

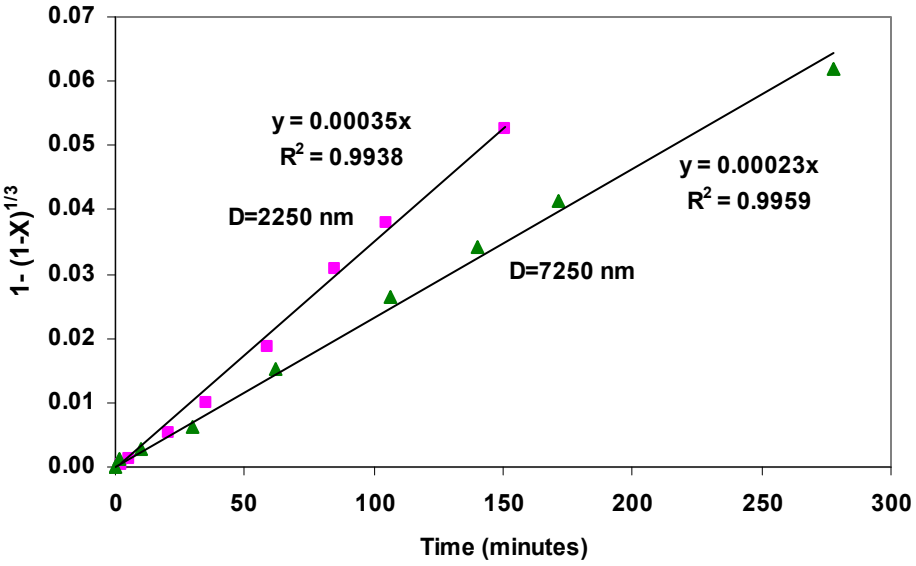


Fig. 7.17 *Shrinking sphere model for the dissolution of gold powder of different particle sizes in copper(II)-ammonia-thiosulfate solutions under nitrogen. [$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.*

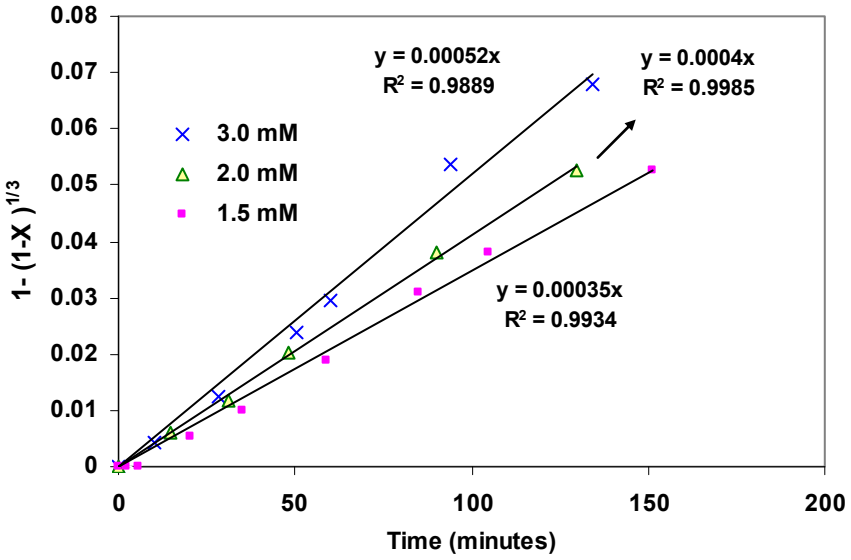


Fig. 7.18 *Shrinking sphere model for the dissolution of gold powder at different copper(II) concentrations in ammonia-thiosulfate solutions under nitrogen.*
[$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Table 7.6 *Rate constant for the dissolution of gold powder based on a shrinking sphere model*

Particle size (μm)	[Cu(II)] (mM)	10^4 k_{ss} (min^{-1})[a]	10^7 k ($m\ s^{-1}$)
7.25 (Fig. 7.17)	1.5	2.3	9.1
2.25 (Fig. 7.17)	1.5	3.5	4.3
2.25 (Fig. 7.18)	2.0	4.0	3.7
2.25 (Fig. 7.18)	3.0	5.2	3.2

a. based on Figs. 7.17 - 7.18.

7.6.3 Effect of oxygenation

The uncertainty of a shrinking sphere or core kinetic model in solutions of high ammonia concentration of 300 mM [NH_3+NH_4^+] has been noted in section 7.6.1 because neither one gave a good linear relationship in Fig. 7.13. However, in the presence of oxygen, the rates of gold dissolution are better described by a shrinking sphere model at higher thiosulfate and ammonia concentrations, as shown in Fig. 7.19. The validity of a shrinking sphere model for a longer period time in the presence of a relatively higher thiosulfate concentration of 50 mM in Fig. 7.19 can be related to the apparently constants steady state of copper(II)-ammonia-thiosulfate concentration under these conditions (Wensveen and Nicol, 2005).

At lower thiosulfate concentrations, the steady state concentration of the copper(II)-ammnia-thiosulfate complex is higher (Wensveen and Nicol, 2005). This is also reflected in Fig. 7.19 at initial stages, showing higher slopes at low thiosulfate concentrations. However, oxygen is continuously consumed in the oxidation of thiosulfate, producing polythionates (Wensveen and Nicol, 2005). This affects gold dissolution, especially at low initial thiosulfate concentrations over a

longer period of time, as shown in Fig. 7.19. The low rates are a result of enhanced thiosulfate consumption in the presence of oxygen. This shows the importance of considering the effect of polythionates on gold dissolution under anaerobic conditions to examine:

(i) the direct involvement of polythionates in the surface reaction, or

(ii) the indirect involvement of polythionates by affecting the copper(II) concentration.

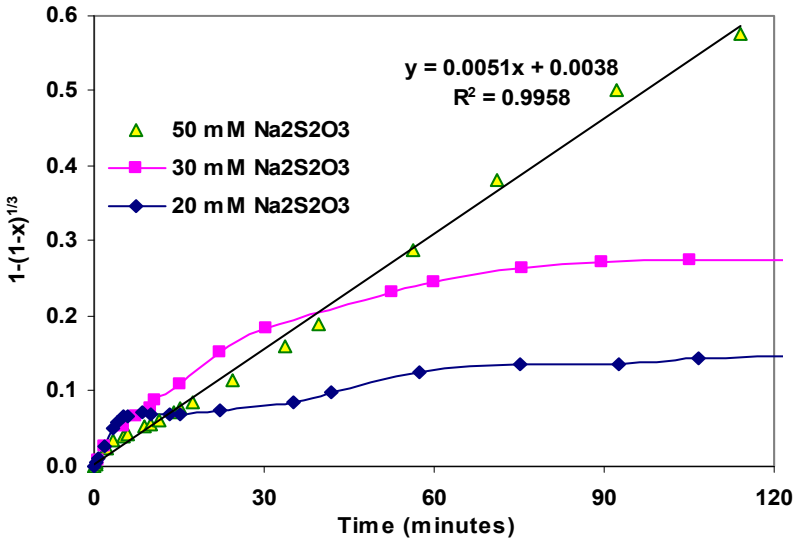


Fig. 7.19 *Shrinking sphere model for the dissolution of gold colloid at different thiosulfate concentrations in oxygenated copper(II)-ammonia solutions. [O_2] = 0.31mM, [Cu(II)] = 2.0 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3.*

7.6.4 Effect of tetrathionate and trithionate

In a recent study, Feng and van Deventer (2007a) showed that the consumption of copper(II) in ammoniacal copper(II)-thiosulfate system is enhanced by the presence of 5-10 mM tetrathionate, while trithionate showed little influence (Fig. 7.20). However, both tetrathionate and trithionate enhanced the thiosulfate concentration from its initial value of 0.1 M to 0.102-0.109 M after 7 hours (Fig. 7.21) due to hydrolysis reactions described in Chapter 2. The effect of these changes on the dissolution of gold (foil) was less significant during the first 2 hours, but beneficial effects were observed after 5 - 6 hours (Fig. 7.22).

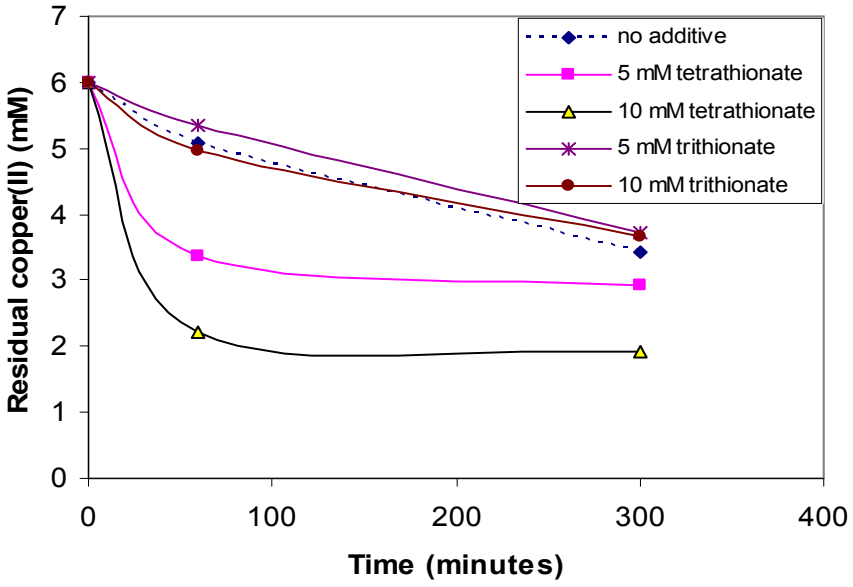


Fig. 7.20 *Effect of tetrathionate or trithionate on residual copper(II) during reaction with thiosulfate.*
Initial conditions: [$Na_2S_2O_3$] = 100 mM, [NH_3+NH_4^+] = 500 mM, [Cu(II)] = 6 mM, 25 ^oC (Feng and van Deventer, 2007a).

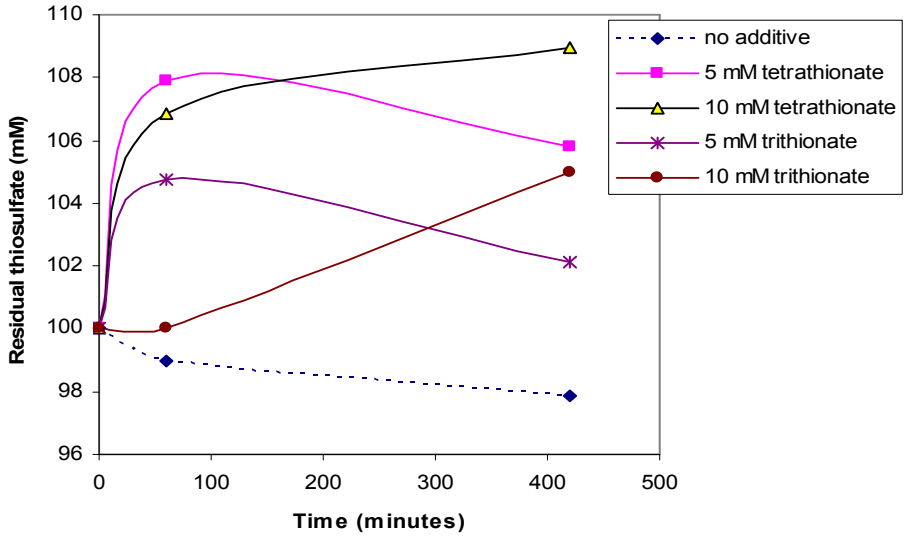


Fig. 7.21 *Effect of tetrathionate or trithionate on residual thiosulfate during reaction of copper(II) with thiosulfate.*
Initial conditions: [$Na_2S_2O_3$] = 100 mM, [NH_3+NH_4^+] = 500 mM, [Cu(II)] = 6 mM, 25 °C (Feng and van Deventer, 2007a).

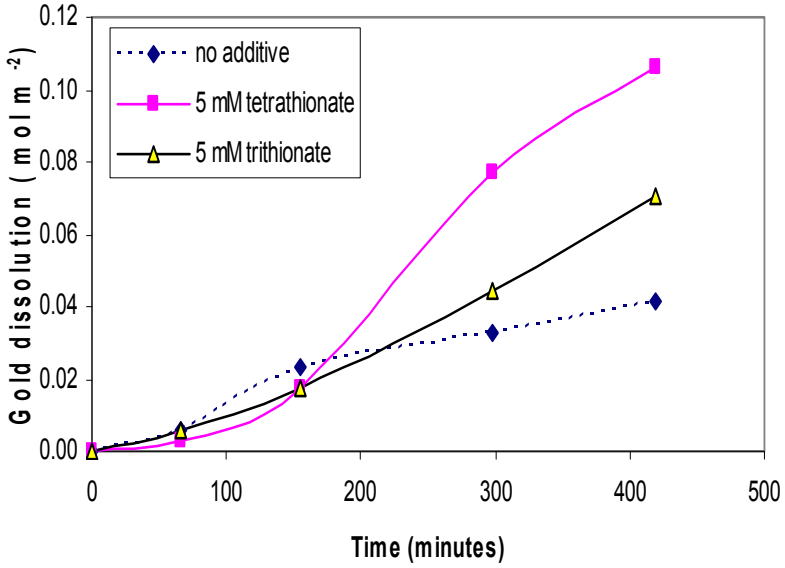


Fig. 7.22 *Effect of tetrathionate or trithionate on the dissolution of gold foil in copper(II)-ammonia-thiosulfate solutions.*
Initial conditions: [$Na_2S_4O_6$] = 5 mM, [$Na_2S_3O_6$] = 5 mM, [$Na_2S_2O_3$] = 100 mM, [NH_3+NH_4^+] = 500 mM, [Cu(II)] = 6 mM, 25 °C (Feng and van Deventer, 2007a).

The results obtained with gold colloids in the presence of 5 mM tetrathionate or 20 mM trithionate in the present study shows the applicability of a shrinking sphere model in both cases (Fig. 7.23). The higher slope of the linear relationship in the presence of trithionate in Fig. 7.23 shows a beneficial effect.

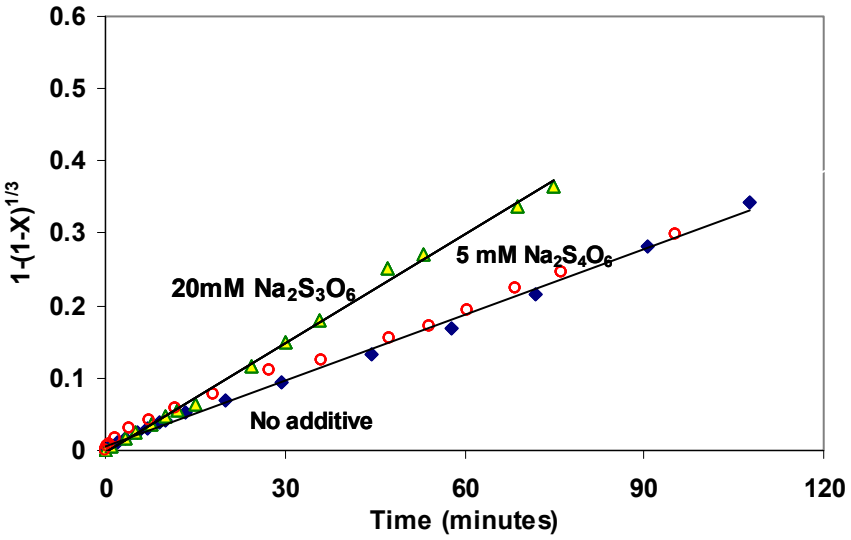


Fig. 7.23 *Shrinking sphere model for the dissolution of gold colloids by copper(II)-ammonia-thiosulfate solutions in the presence of trithionate or tetrathionate under nitrogen.*
[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5

Figure 7.24 shows the change in tetrathionate and trithionate concentration as well as the extent of gold dissolution from gold foil. These experiments were conducted using a solution of 0.165 M $(NH_4)_2S_2O_3$, 0.5 M NH_3, and 0.8 mM copper(II) at 25 ^oC (Feng and van Deventer, 2007c). It is clear that although the concentration of tetarthionate and trithionate increased with time the rate of gold dissolution shown by the gradient of the linear relationship did not change with time when the dissolution of gold foil was carried out at a flow rate of 10 ml nitrogen per minute.

Figure 7.25 shows that oxygen injection at a rate of 10 ml per minute increases the rate of gold dissolution. However, the slope of both lines is close to 4 $x10^{-5}$ mol m^{-2} min^{-1}. This corresponds to a rate of 6.7 x 10^{-7} mol m^{-2} s^{-1}, which is comparable with the initial rates of the dissolution of gold colloids in the presence or absence of oxygen reported in Table 7.4. Assuming that the rate can be expressed by R = k[Cu(II)], and substituting [Cu(II)] = 0.8 mol m^{-3} (Fig. 7.24), the value of the rate constant k appears to be 8.3 x 10^{-7} m s^{-1} for the dissolution of gold foil. This value is of the same order as the values of rate constant for gold powder based on the shrinking sphere model reported in Table 7.6.

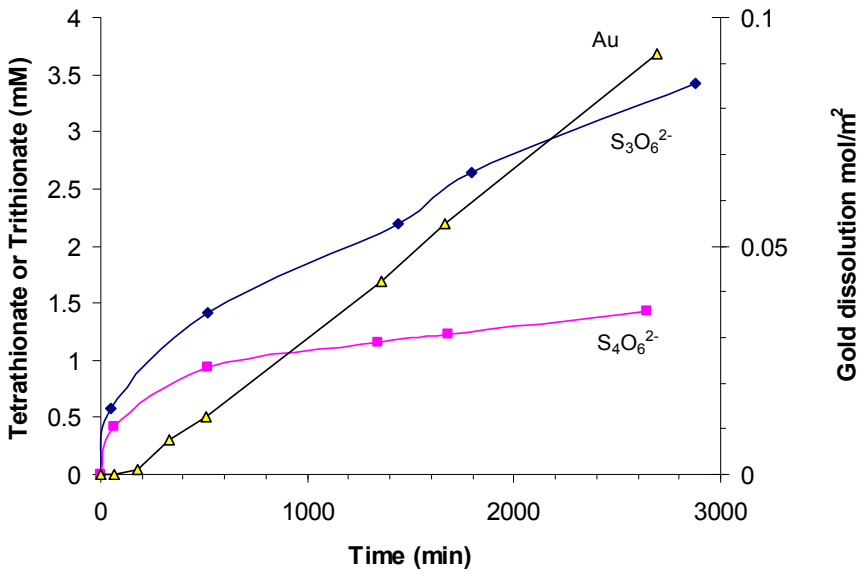


Fig. 7.24 *Formation of tetrathionate and trithionate during the dissolution of gold foil by copper(II)-ammonia-thiosulfate solutions under nitrogen. $[(NH_4)_2S_2O_3]$ = 0.165 M; $[NH_3]$ = 0.5 M, [Cu(II)] = 0.8 mM; 25 °C; nitrogen flow rate 10 ml min^{-1}. (Data from Feng and van Deventer, 2007c).*

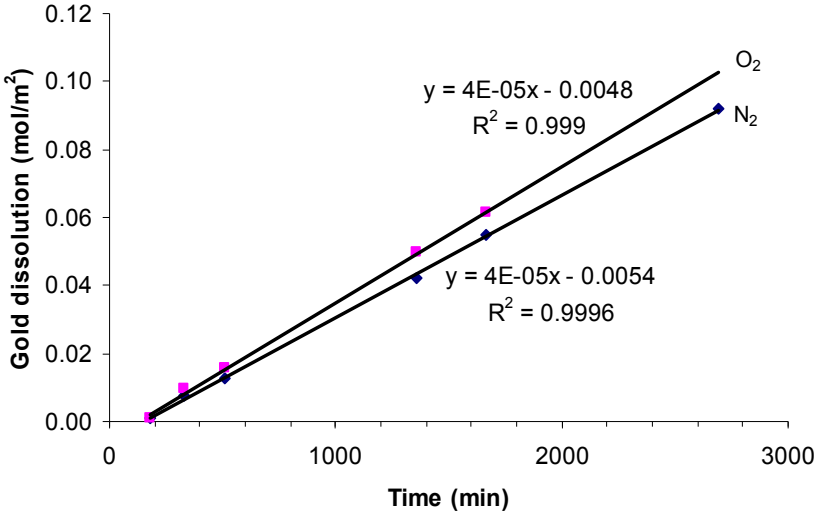


Fig. 7.25 *Effect of oxygenation on dissolution of gold foil (Conditions same as in Fig.7.24; Data from Feng and van Deventer, 2007c).*

7.6.5 Effect of lead(II), silver(I), chloride and ammonia

A shrinking sphere kinetic model is applicable for the dissolution of colloidal gold in the presence of additives such as lead nitrate, silver nitrate and sodium chloride. Although lead(II) ions have no significant effect on the slope of the linear relationship, Fig. 7.26 shows a positive effect caused by silver nitrate. The slope of linear relationships increase with increase in silver nitrate concentration.

Likewise, Figs. 7.27 and 7.28 show that an increase in sodium chloride or ammonia concentration increases the slope of the linear relationships. These results suggest the direct involvement of Ag(I), Cl^- and NH_3 in the surface reaction as noted previously. Fig. 7.29 shows a log-log plot of k_{ss} versus [X], for X = Ag(I), Cl^-, or NH_3. The reaction orders based on gradients of linear relationships are listed in Table 7.7.

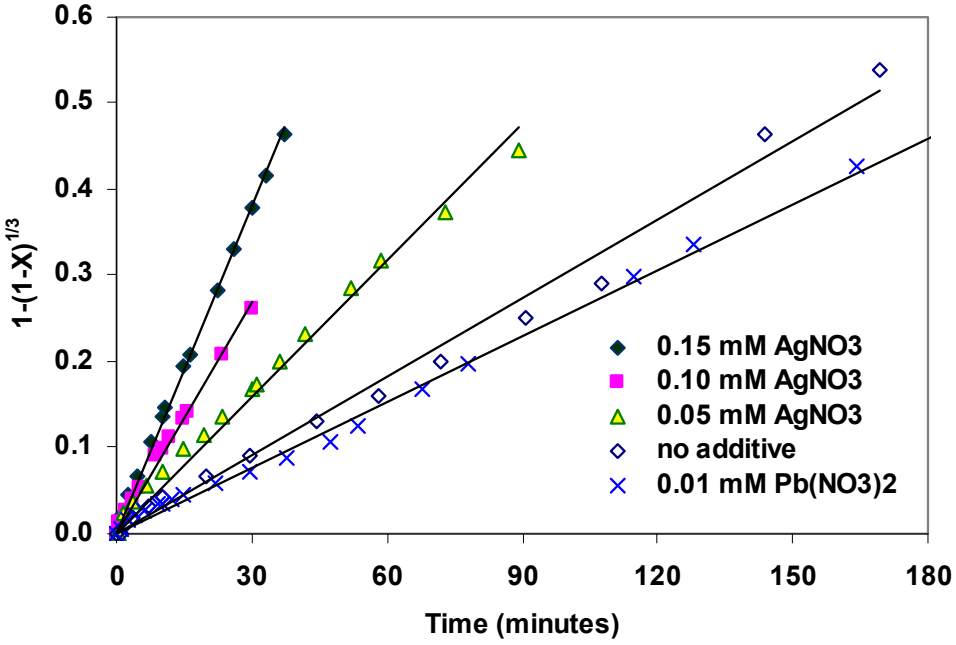


Fig. 7.26 *Shrinking sphere model for the dissolution of gold colloids by copper(II)-ammonia-thiosulfate solutions in the presence of silver(I) under nitrogen. [Cu(II)] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.*

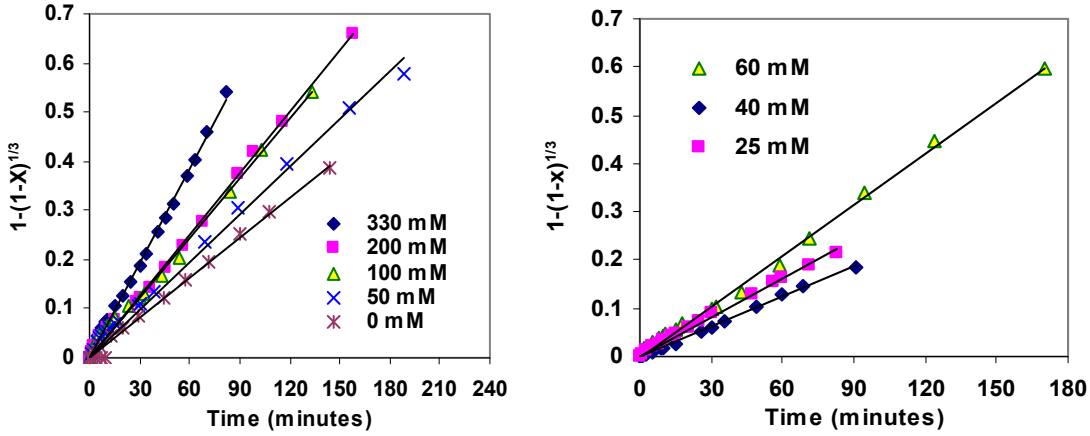


Fig. 7.27 *Shrinking sphere model for the dissolution of gold colloids by copper(II)-ammonia-thiosulfate solutions in the presence of sodium chloride under nitrogen.*

[Cu(II)] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Fig. 7.28 *Shrinking sphere model for the dissolution of gold colloids by copper(II)-thiosulfate solutions at different ammonia concentrations under nitrogen. [Cu(II)] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, pH = 9.3.*

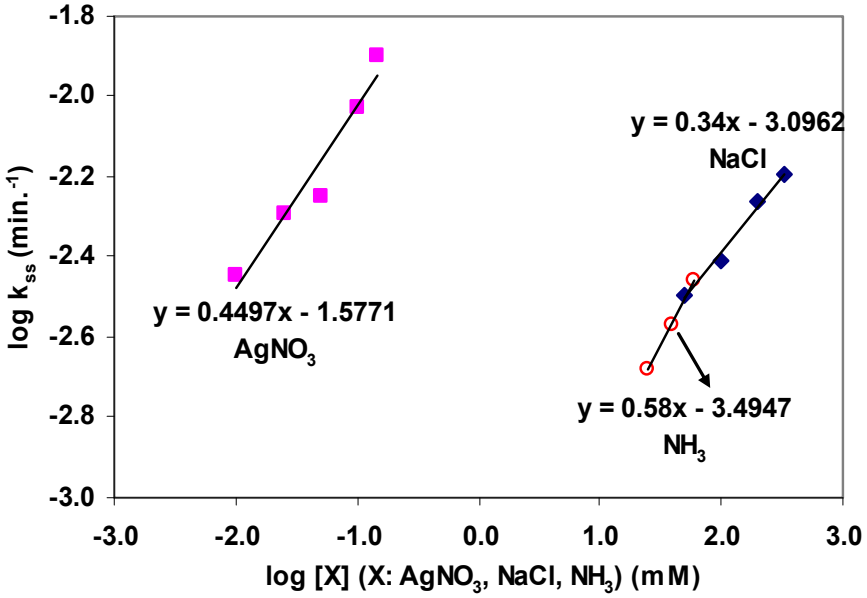


Fig. 7.29 *Logarithmic plot of apparent rate constant as a function of silver(I), chloride, or ammonia concentration in copper(II)-ammonia-thiosulfate solutions under nitrogen.*

Table 7.7 *Reaction orders for the dissolution of gold colloid by copper(II) based on apparent rate constants*

[Cu(II)] (mM)	[$Na_2S_2O_3$] (mM)	[NH_3+NH_4^+] (mM)	pH	Additive	[Additive] (mM)	Order
1.5	20	50-120	9.3			$[NH_3]^{0.58, a}$
1.5	20	120	9.5	NaCl	0[b]-330	$[NaCl]^{0.34}$
1.5	20	120	9.5	$AgNO_3$	0.010-0.15	$[AgNO_3]^{0.45}$

25°C, under nitrogen.

a. [NH_3+NH_4^+] >180 mM do not fit into any of the models.

b. At [NaCl] = 0 mM, the solution of gold colloid prepared using $NaAuCl_4$, which contains 0.4 mM Cl^-.

The near half order dependence of k_{ss} on concentrations of silver nitrate shown in Fig.7.29 indicates electrochemical nature of the reaction between gold and silver(I) as expressed in Eqs. 7.19 and 7.20:

$Au + Ag(I) = Au(I) + Ag$ (slow, rate controlling) (7.19)

$Cu(II) + Ag = Cu(I) + Ag(I)$ (fast) (7.20)

Table 7.8 lists the stability constants of silver(I) and gold(I) complexes formed in ammonia-thiosulfate solutions. Fig. 7.30 shows the effect of silver(I) concentration on species distribution. It can be seen that $Ag(S_2O_3)_2^{3-}$ is the predominant complex in all cases. As noted in Chapter 2, the calculation of equilibrium constants for possible reactions involved in gold-silver leaching systems is hampered by two factors: (i) association of the anion $S_2O_3^{2-}$, with cations such as Na^+ , NH_4^+, $Cu(I)(NH_3)_2^+$, and $Cu(II)(NH_3)_4^{2+}$, leading to the formation of ion-pairs or mixed complexes such as $NaS_2O_3^-$, $NH_4S_2O_3^-$ (Senanayake 2004), $Cu(I)(NH_3)(S_2O_3)^-$ (Black, 2006), $Cu(II)(NH_3)_m(S_2O_3)^0$ (Byerley et al., 1973; Wensween, 2005), and (ii) formation of mixed metal-ligand complex species such as $Ag(I)Au(I)(S_2O_3)_n$ or Au-Ag alloys (Webster, 1986). Ignoring such complications, Table 7.9 lists the general reactions which can be involved in the leaching of silver metal and cementation of silver onto gold in thiosulfate solutions. The higher equilibrium constants reveal that the oxidation of silver by copper(II) is thermodynamically more favourable when both copper(I) and silver(I) form complexes with thiosulfate (R4-R7). In comparison, the cementation of silver onto gold is less favourable when silver(I) is in the form of thiosulfate complexes (R8-R10).

Table 7.8 *Stability constants of gold and silver complexes at 25°C*

Reaction			K*
$Ag^+ + NH_3$	=	$Ag(NH_3)^+$	$10^{3.6}$
$Ag^+ + 2NH_3$	=	$Ag(NH_3)_2^+$	$10^{7.0}$
$Ag^+ + S_2O_3^{2-}$	=	$Ag(S_2O_3)^-$	$10^{8.97}$
$Ag^+ + 2S_2O_3^{2-}$	=	$Ag(S_2O_3)_2^{3-}$	$10^{13.1}$
$Ag^+ + NH_3 + S_2O_3^{2-}$	=	$Ag(NH_3)(S_2O_3)^-$	$10^{10.6}$
$Au^+ + 2S_2O_3^{2-}$	=	$Au(S_2O_3)_2^{3-}$	10^{24}
$Au^+ + NH_3 + S_2O_3^{2-}$	=	$Au(NH_3)(S_2O_3)^-$	10^{20}

*Data from Perera and Senanayake (2004).

Table 7.9 *Standard Gibbs free energy values ($\Delta G^o_{f,\ 298\ K}$) and equilibrium constants for silver and gold dissolution*

Reaction	ΔG^o_f* (kJ/mol)	K
R1. $Ag + Cu(NH_3)_4^{2+} = Ag(NH_3)_2^+ + Cu(NH_3)_2^+$	63.2	8.4×10^{-12}
R2. $Ag + Cu(NH_3)_4^{2+} + 2S_2O_3^{2-} = Ag(S_2O_3)_2^{3-} + Cu(NH_3)_2^+ + 2NH_3$	33.1	1.6×10^{-6}
R3. $Ag + Cu(NH_3)_4^{2+} + 3\ S_2O_3^{2-} = Ag(S_2O_3)_3^{5-} + Cu(NH_3)_2^+ + 2NH_3$	25.6	3.2×10^{-5}
R4. $Ag + Cu(NH_3)_4^{2+} + 4\ S_2O_3^{2-} = Ag(S_2O_3)_2^{3-} + Cu(S_2O_3)_2^{3-} + 4NH_3$	-7.70	2.2×10^{1}
R5. $Ag + Cu(NH_3)_4^{2+} + 5\ S_2O_3^{2-} = Ag(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3$	-16.1	6.5×10^{2}
R6. $Ag + Cu(NH_3)_4^{2+} + 5\ S_2O_3^{2-} = Ag(S_2O_3)_3^{5-} + Cu(S_2O_3)_2^{3-} + 4NH_3$	-15.2	4.6×10^{2}
R7. $Ag + Cu(NH_3)_4^{2+} + 6\ S_2O_3^{2-} = Ag(S_2O_3)_3^{5-} + Cu(S_2O_3)_3^{5-} + 4NH_3$	-23.6	1.4×10^{4}
R8. $Au + Ag(NH_3)_2^+ + 2\ S_2O_3^{2-} = Ag(S_2O_3)_2^{3-} + Ag + 2NH_3$	-30.1	1.9×10^{5}
R9. $Au + Ag(S_2O_3)_2^{3-} = Au(S_2O_3)_2^{3-} + Ag$	8.4	3.3×10^{-2}
R10. $Au + Ag(S_2O_3)_3^{5-} = Au(S_2O_3)_2^{3-} + Ag + S_2O_3^{2-}$	15.9	1.6×10^{-3}

* Data from Aylmore and Muir, 2001.

The calculated values of electrode potentials based on the Nernst equation $E\{Ag^+/Ag^0\} = E^o\{Ag^+/Ag^0\} + RT\ ln[Ag^+]$ are shown in Fig. 7.31 assuming unit activity of silver metal (a_{Ag} = 1). These values are lower than the calculated gold(I)/gold(0) potentials at lower concentrations of silver(I), indicating that the cementation of pure silver according to reactions R8 - R10 in Table 7.9 is thermodynamically not feasible under such conditions. However, the substitution of a lower activity of silver (a_{Ag} = 0.1), assuming the formation of alloys, gives higher potentials which makes the cementation thermodynamically feasible at the range of silver(I) and gold(I) concentrations considered in the present study. This suggests the possibility of silver cementation on gold surface.

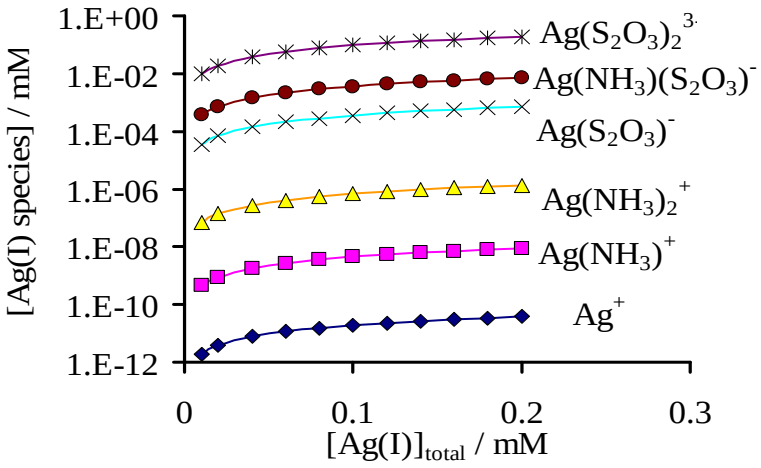


Fig. 7.30 *Effect of silver(I) concentration on silver(I) speciation at 25 °C. (Conditions same as in Fig. 7.26, thermodynamic data from Table 7.8).*

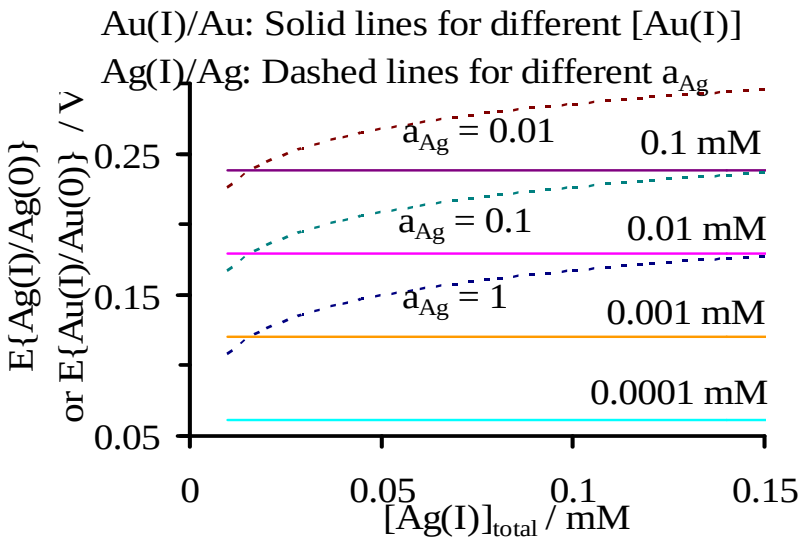


Fig. 7.31 *Comparison between calculated silver(I)/silver(0) and gold(I)/gold(0) potentials at different silver(I) and gold(I) concentrations. EAg(I)/Ag(0) based on the Nernst equation and Ag^+ concentration, $E^oAg^+/Ag(0)$ = 0.799 V). Predominant complex species $M(I)(S_2O_3)_2^{3-}$. (Dotted lines for different activity of silver in gold (alloy)).*

Table 7.10 lists the results showing the effect of sodium nitrate and silver nitrate on apparent rate constants based on a shrinking particle model. The initial rates per unit area based on the relationship $R = k_{ss}\ r\ \rho$ (Senanayake, 2007) are also listed in Table 7.10. Fig. 7.32 shows a plot of R as a function of [$AgNO_3$], [Ag(c)] or [$NaNO_3$]. The linear relationships of the two lines in Fig. 7.32 give a y-intercept of 0.5 x 10^{-7} mol m^{-2} s^{-1} for the rate of dissolution of colloidal gold at zero concentration of $AgNO_3$ and $NaNO_3$. This value is close to the value of 1 x 10^{-7} mol m^{-2} s^{-1} reported for stabilized colloids of different particle sizes in Table 6.6, in the absence of additives. The small variation in k_{ss} and rate with increasing concentration of sodium nitrate in Table 7.10 and Fig. 7.32, indicates that nitrate ions have no significant effect on gold dissolution. It is of interest to

note that the effect of 0.1 mM silver nitrate on the rate of gold dissolution is comparable with that of 0.1 mM silver colloid (Fig. 7.32).

Table 7.10 *Effect of sodium and silver nitrates on apparent rate constants and rates*

[Additive]	(mM)	10^4 k_{ss} (min^{-1})	10^7 R (mol m^{-2} s^{-1})
$NaNO_3$	*0*	*31*	*0.51*
	50	*32*	*0.52*
	100	*33*	*0.54*
	200	*35*	*0.57*
	330	*37*	*0.60*
$AgNO_3$	*0.01*	*36*	*0.59*
	0.025	*46*	*0.75*
	0.05	*53*	*0.86*
	0.10	*79*	*1.3*
	0.15	*127*	*2.1*

$R = k_{ss}\ r\ \rho$; k_{ss} based on slopes as in Fig. 7.26; and similar plots drawn for results in the presence of $NaNO_3$ (see Appendix A3.2).

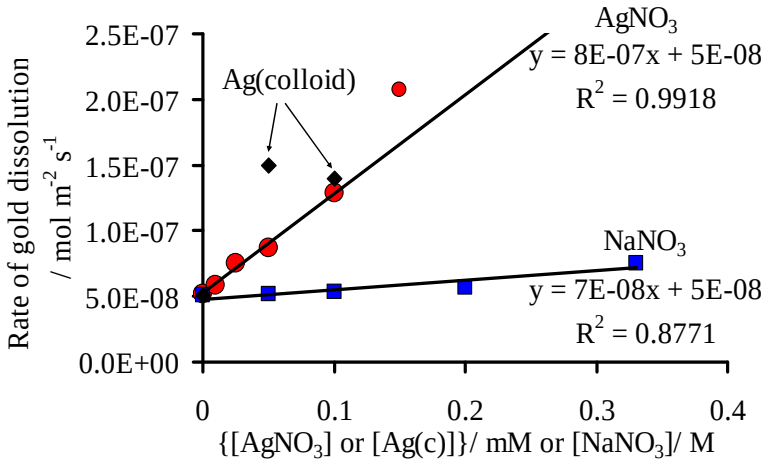


Fig. *7.32. Logarithmic plot of apparent rate constants as a function of reagent concentration (data from Table 7.10).*

The apparent involvement of silver(I) in the surface reaction (Fig. 7.26) and the faster dissolution of silver than gold (Fig. 4.9), as well as the surface chemical controlled reaction for the dissolution of gold-silver alloy evident from Fig. 6.9 (curves A and B) may be used to propose a surface reaction mechanism for the beneficial effect of silver on gold dissolution. The role of silver(I) appears to be in the form of a redox mediator according to the rate controlling reaction:

Au + Ag(I) = Au(I) + Ag, followed by the fast dissolution of silver according to the reaction Ag + Cu(II) = Ag(I) + Cu(I), described in Eqs. 7.19 and 7.20.

Silver(I) and chloride ions may also be involved in the surface reaction by avoiding the passivating sulfur layer. Further discussion of the beneficial effect of silver(I) and chloride ions is beyond the scope of this thesis due to the lack of information on activity coefficients and stability constants of the relevant complexes including mixed Au^{+}-Ag^{+}-$S_2O_3^{2-}$, complexes, and alloy formation.

7.7 Summary and conclusions

The dissolution of gold powder by copper(II) in oxygen-free solutions follows the same trend as that of gold colloid. Initial dissolution rates of gold powder and colloids show a reaction order of about 0.5 with respect to copper(II) concentration in oxygen free solutions. The reaction orders were about 0.5 for the variation of initial rates with respect to thiosulfate and ammonia at low concentrations for gold colloids. The half order mechanisms can be rationalised on the basis of an electrochemical mechanism. However, in oxygenated copper(II) solutions the reaction order is close to unity with respect to copper(II) at low concentrations in the case of gold colloids, massive gold and gold-silver alloys.

Results obtained in experiments conducted at relatively low concentrations of thiosulfate and ammonia favour a shrinking sphere model for the dissolution of gold colloids and powder in oxygen-free copper(II)-ammonia-thiosulfate solutions. This is further supported by a linear relationship between the apparent rate constant (k_{ss}, s^{-1}) and the reciprocal of the radius of gold colloids. Slightly higher rate constants for gold powders and foil portray a higher surface roughness factor of massive gold, compared to both stabilized and unstabilized gold colloids.

Both initial rates and apparent rate constants for the dissolution of gold colloids and powders by copper(II) are enhanced by the presence of silver nitrate and

sodium chloride, showing the involvement of these ions in the surface reaction, possibly by interfering with a sulfur containing surface passivating film. The apparent rate constant based on a shrinking sphere model is unaffected by the presence of sodium nitrate, lead nitrate or sodium tetrathionate, but is slightly enhanced by the presence of sodium trithionate. The beneficial effect of silver(I) appears to be due to its role as a redox mediator where the cementation of silver on to gold surface is followed by the fast dissolution of silver metal (or alloy) by copper(II).

CHAPTER 8 SUMMARY AND RECOMMENDATIONS

8.1 Summary

The dissolution rates of gold colloids depend on the type of reagents (oxidants and ligands) and other background electrolytes, reaction products, as well as the physico- chemical factors such as particle size and temperature. A summary of the findings in thesis is presented below:

1. The relative rates and the extent of gold dissolution at 25ºC in different lixiviant systems in a given time interval are of the order: oxygen-cyanide > copper(II)-ammonia-thiosulfate ≈ oxygen-copper(II)-ammonia-thiosulfate > oxygen-ammonia-thiosulfate ≥ oxygen-ammonia > copper (II)-ammonia.

2. The complex $Au(S_2O_3)_2^{3-}$ has been identified to be the predominant gold(I) species in lixiviant solutions containing oxygen or copper(II) as oxidant and thiosulfate or mixed ammonia-thiosulfate as ligands. In the absence of thiosulfate, the measured gold potentials are in good agreement with those reported for the $Au(NH_3)_4^{3+}/Au(NH_3)_2^{+}$ couple, indicating that disproportionation or oxidation of $Au(NH_3)_2^{+}$ occurs during the dissolution. During the reaction of copper(II) with thiosulfate in ammonia solution without oxygen, the measured platinum electrode potentials represent the redox couple of $Cu(NH_3)_n^{2+}/Cu(S_2O_3)_m^{1-2m}$ (n = 4 or 3, m = 3 or 2), depending on the concentrations of thiosulfate and ammonia.

3. The initial rates of gold dissolution in oxygen-ammonia-thiosulfate solutions show a reaction order of 0.28 with respect to the concentration of dissolved oxygen, independent of concentration of ammonia and thiosulfate. An activation energy of 25 kJ/mol in the temperature range 25ºC to 48ºC indicated a diffusion controlled reaction. Initial rates show a reaction order of 0.33 with respect to ammonia in the absence of thiosulfate.

4. Gold dissolution in ammoniacal copper(II) thiosulfate solutions under nitrogen had an activation energy of 40-50 kJ mol^{-1} for the temperature range 22^{o}C to 48^{o}C. This suggests the involvement of a mixed chemically/diffusion controlled surface reaction.

5. The dissolution of gold powder by copper(II) in oxygen-free solutions followed the same trend as that of gold colloid. Initial dissolution rates of gold powder and colloids showed a reaction order of about 0.5 with respect to copper(II) concentration in oxygen free solutions. The reaction orders for the dissolution of gold colloids were about 0.5 based on the variation of initial rates with respect to thiosulfate and ammonia at low concentrations. However, in oxygenated copper(II) solutions, the reaction order was close to unity with respect to copper(II) at low concentrations, in the case of gold colloids, massive gold and gold-silver alloys. The half order reactions between gold and copper(II) can be rationalised on the basis of an electrochemical model. High oxygen concentration in solution had a negative effect on the initial rate of dissolution and percentage dissolution of gold.

6. Relatively low concentrations of thiosulfate and ammonia favoured a shrinking sphere model for the dissolution of gold colloids and powder in oxygen-free copper(II)-ammonia-thiosulfate solutions. This was further supported by a linear relationship between the apparent rate constant (k_{ss}, s^{-1}) and the reciprocal of the radius of gold colloids. Slightly higher rate constants for gold powders and foil showed a higher surface roughness factor of massive gold.

7. Both initial rates and apparent rate constants for the dissolution of gold colloids and powders by copper(II) were enhanced by the presence of silver nitrate and sodium chloride showing the involvement of silver(I) and chloride ions in the surface reaction. Silver ions is likely to react with sulfur species and catalyse gold oxidation; chloride ions possibly by interfering with a passivating sulfur rich film on gold surface. The dependence of rate on initial concentration of silver nitrate or sodium chloride showed reaction orders of 0.45 - 0.8 and 0.34 respectively. The apparent rate constant, based on a shrinking sphere model, was unaffected by the presence of sodium nitrate, lead nitrate or sodium tetrathionate, but slightly enhanced by the presence of sodium trithionate. However, the presence of sodium carbonate and sodium sulfite showed significant negative effects on the apparent rate constant, indicating the association/reaction of copper(II) with these anions.

8. The copper(II)-ammonia-thiosulfate solution in the absence of oxygen or in the presence of oxygen is the best system for dissolving gold based on the results. In the absence of oxygen, copper 1.5-4.5 mM, thiosulfate 20-50 mM,

ammonia 120-300 mM and pH 9.3-10 are the best conditions. The presences of carbonate and sulfite have a significant negative effect on the dissolution of gold. The presence of sodium trithionate shows a beneficial effect in the first two hours, while sodium tetrathionate or lead nitrate have a small negative effect and sodium nitrate showed no effect on the dissolution of gold. In the presence of oxygen, copper 2.0-3.0 mM, thiosulfate 50 mM, ammonia 240 mM and pH 9.3-9.5 are the best conditions.

9. The dissolution of gold by oxidation with copper(II) in oxygen-free solutions appears to be a result of the reaction between gold, thiosulfate ions, and the mixed complex $Cu(NH_3)_p(S_2O_3)^0$.

8.2 Recommendations for further work

- Analysis of rate data on the basis of actual speciation which takes into account the copper(I), copper(II) and various sulfur containing species as well as the ion associates such as $NaS_2O_3^-$ and $NH_4S_2O_3^-$.
- The role of excess oxygen on the basis of the effect of oxygen on copper(I), copper(II), and sulfur speciation.
- The role of silver and chloride in gold dissolution mechanism.
- Effect of other gold ligands and higher temperatures.
- Extension of this work to non-ammoniacal solutions.
- Extension of this work to gold powders, ores, and concentrates.

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APPENDIX

APPENDIX A1

Table A1.1 *Comparison between measured and calculated absorbance for the mixture of gold colloid and copper(II)-ammonia solution.*

[Cu(II)] (mM)	$[NH_3]$ (mM)	$[(NH_4)_2SO_4]$ (mM)	$A\{Cu(NH_3)_4^{2+}\}_{530nm}$ / $A\{Au(c)\}_{530nm}$	A^a	A^b	Error %
0	100	70	0.002 / 0.801	0.803	0.805	0.2
0.5	100	70	0.032 / 0.801	0.833	0.83	0.4
1.0	100	70	0.063 / 0.800	0.863	0.861	0.2
1.5	100	70	0.094 / 0.790	0.884	0.876	0.9
2	100	70	0.124 / 0.801	0.925	0.919	0.7
3	100	70	0.183 / 0.798	0.981	0.978	0.3
0	20	0	0 / 0.780	0.780	0.781	0.1
1	90	0	0.028 / 0.782	0.810	0.802	1.0
3	20	20	0.064 / 0.770	0.834	0.832	0.2
10	900	0	0.275 / 0.782	1.057	1.049	0.8

[Au(c)] = 0.1 mM.

A^a $A\{Cu(NH_3)_4^{2+}\}_{530\ nm}$ +A $\{Au(c)\}_{530nm}$ calculated.

A^b $A\{Au(c) + Cu(NH_3)_4^{2+}\}_{530\ nm}$ measured.

APPENDIX A2 Initial dissolution rates of gold colloid (R_i)

Table A2.1 *Initial dissolution rates of gold colloid (R_i) and reaction orders in oxygenated ammonia-thiosulfate solutions: effect of reagent concentration*

$[Na_2S_2O_3]$ (mM)	$[NH_3+NH_4^+]$ (mM)	[NaCl] (mM)	pH	R_i (μM/min.)	Slope of logR_i versus log[X]
0	67	0	9.5	0.39	0.33
	100			0.43	
	150			0.55	
	200			0.57	
	280			0.60	
20	67	0	9.5	0.81	0
	100			0.9	
	150			0.72	
	200			0.71	
	300			0.65	
	500			0.57	
10	0	0	9.3	1.9	0
30				1.8	
50				2.1	
70				2.0	
10	200	0	9.5	1.0	0
20				0.79	
30				0.8	
50				0.79	
70				0.95	
20	120	0	9.5	1.5	0
		50		1.4	
		100		1.3	
		200		1.6	
		330		1.1	
30	0	0	9.5	1.4	0
		50		1.1	
		100		0.87	
		200		1.6	
		330		1.2	
0	120	50	9.5	0.68	0
		100		0.75	
		200		0.59	
		330		0.68	

$[O_2]$ = 0.25 mM at 25ºC.

Table A2.2 *Initial dissolution rates of gold colloid (R_i) and reaction orders in copper(II)-ammonia-thiosulfate solutions: effect of reagent concentration*

[Cu(II)] (mM)	[$Na_2S_2O_3$] (mM)	[NH_3+NH_4^+] (mM)	pH	R_i (μM /min.)	10^6 R_i mol m^{-2} S^{-1}	Slope of logR_i versus log[X]
0.5	0	120	9.5	0.4	0.022	0
1.0				0.4	0.022	
1.5				0.3	0.017	
2.5				0.3	0.017	
0.5	50	240	9.3	2.4	0.13	0.41
1.0				3.1	0.17	
1.5				3.7	0.21	
2.0				4.1	0.23	
3.0				4.7	0.26	
4.5				6.0	0.33	
1.5	10	240	9.3	1.7	0.094	0.49
	20			2.6	0.14	
	30			3.0	0.17	
	50			3.7	0.21	
	70			3.7	0.21	
	95			3.7	0.21	
1.5	0	60	9.3	0.3	0.017	0
		120		0.3	0.017	
		180		0.2	0.011	
		240		0.2	0.011	
1.5	20	80	9.3	1.4	0.078	0.60
		120		1.9	0.11	
		180		2.4	0.13	
		240		2.7	0.15	
		300		2.7	0.15	
		420		2.7	0.15	
		540		2.65	0.15	
		580		2.60	0.14	
2.0	40	240	8.90	2.1	0.12	0.47
			9.05	2.6	0.14	
			9.3	3.0	0.17	
			9.6	3.2	0.18	
			10.0	3.2	0.18	
			11.0	3.1	0.17	

Table A2.3 *Initial dissolution rates of gold colloid (R_i) and reaction orders in copper(II)-ammonia-thiosulfate solutions*: *effect of reagent concentration*

Salts	Concentration (mM)	$[Na_2S_2O_3]$ (mM)	R_i (μM/min.)	$10^6 R_i$ mol m^{-2} S^{-1}	Slope of logR_i versus log[X]
$NaNO_3$	0	20	2.1	0.12	0
	50		2.1	0.12	
	100		2.1	0.12	
	200		2.1	0.12	
	330		2.2	0.12	
NaCl	0	0	0.64	0.036	
	50		0.85	0.047	0.15
	100		0.96	0.053	
	200		1.07	0.059	
	330		1.12	0.062	
NaCl	50	20	2.5	0.14	0.15
	100		2.8	0.16	
	200		3.0	0.17	
	330		3.35	0.19	
$AgNO_3$	0.01	20	2.45	0.14	0.22
	0.025		2.9	0.16	
	0.05		3.2	0.18	
	0.1		3.9	0.22	
	0.15		4.2	0.23	
Ag colloid	0	20	2.0	0.11	
	0.05		2.7	0.15	0
	0.10		2.5	0.14	
	0.10		2.3	0.13	
$Na_2S_4O_6$	5	20	1.7	0.094	-
$Na_2S_3O_6$	20	20	1.7	0.094	-
$Pb(NO_3)_2$	2 ppm	20	1.8	0.10	-
Na_2CO_3	110	20	2.0	0.11	-
Na_2SO_3	40	20	0.4	0.022	-

[Cu(II)] = 1.5 mM, $[NH_3+NH_4^+]$ = 120 mM, pH = 9.5.

Table A2.4 *Initial dissolution rates of gold colloid (R_i) and reaction orders in oxygenated copper(II)-ammonia-thiosulfate solutions : effect of reagent concentration*

$[O_2]$ (mM)	[Cu(II)] (mM)	$[Na_2S_2O_3]$ (mM)	pH	R_i (μM/ min.)	$10^6 R_i$ mol m^{-2} S^{-1}	Slope of logR_i versus log[X]
0	1.5	50	9.5	3.6	0.20	
0.06-0.25*				3.6	0.20	
0.50				3.0	0.17	
0.63				1.9	0.11	
0.31	1.0	50	9.3	1.5	0.083	1.0
	2.0			3.0	0.17	
	3.0			4.4	0.24	
0.31	2.0	20	9.3	5.4	0.30	-0.64
		30		4.1	0.23	
		50		3.0	0.17	

$[NH_3+NH_4^+]$ = 0.24 M. * Open to air.

Table A2.5 *Effect of temperature*

Temp. °C	$[O_2]$ (mM)	[Cu(II)] (mM)	$[NH_3+NH_4^+]$ (mM)	$[Na_2S_2O_3]$ (mM)	R_i (μM/ min.)	$10^6 R_i$ mol m^{-2} S^{-1}
25	0.56	0	120	20	0.41	0.023
30					0.89	0.04
40					0.93	0.052
48					1.0	0.056
22	0	2.0	240	50	4	0.22
30					6.1	0.34
40					10.2	0.57
48					15.1	0.84

pH = 9.5.

APPENDIX A3 Apparent rate constants for shrinking core and shrinking sphere model

Table A3.1 *Apparent rate constants for shrinking core and shrinking sphere models in copper(II)-ammonia-thiosulfate solutions*

Cu(II) (mM)	$[Na_2S_2O_3]$ (mM)	$[NH_3+NH_4^+]$ (mM)	pH	$10^4 \times k_{sc}$ (min^{-1})	$10^4 \times k_{ss}$ (min^{-1})	Slope of log (k_{sc} or k_{ss}) versus log[X]
1.5	20	50	9.3	-	21	0.58
		80		-	27	
		120		-	35	
		180		6.9*	-	
		240		8.5*	-	
		0.30		-	-	
		0.42		-	-	
		540		-	-	
		580		-	-	

At 25°C. * Initial reaction period.

Table A3.2 *Apparent rate constants for shrinking sphere model in copper(II)-ammonia-thiosulfate solutions*

salt	Concentration (mM)	10^4 x k_{ss} (min^{-1})	Slope of log k_{ss} versus log[X]
$NaNO_3$	0	31	
	50	32	0.05
	100	33	
	200	35	
	330	37	
NaCl	0	32	
	50	32	0.34
	100	40	
	200	42	
	330	74	
$AgNO_3$	0	32	
	0.01	36	
	0.025	46	0.49
	0.05	53	
	0.10	79	
	0.15	127	
$Na_2S_4O_6$	5	26(32)	
$Na_2S_3O_6$	20	50	
$Pb(NO_3)_2$	2 ppm	26	
Na_2CO_3	110	-	
Na_2SO_3	40	-	

[Cu(II)] = 1.5 mM, [NH_3+NH_4^+] = 120 mM, [$Na_2S_2O_3$] = 20 mM, pH 9.5 at 25 ^oC.

Table A3.3 *Apparent rate constants for shrinking sphere model in oxygenated copper(II)-ammonia-thiosulfate solutions*

$[O_2]$ (mM)	Cu(II) (mM)	$[Na_2S_2O_3]$ (mM)	pH	10^4 x k_{ss} (min^{-1})	Slope of log k_{ss} versus log[X]
0.06-0.25**	1.5	50	9.5	102*	
0.50				-	
0.63				45	
0.31	1.0	50	9.3	24	1.14
	2.0			52	
	3.0			84	
0.31	2.0	20	9.3	141*	
		30		135*	
		50		117*	
		50		52	

$[NH_3+NH_4^+]$ = 240 mM at 25 °C.

*Initial 10 min. reaction period. ** Open to air.

Table A3.4 *Apparent rate constants for shrinking sphere model in copper(II)-ammonia-thiosulfate solutions: effect of particle size of gold colloid and gold powder*

Particle Size (nm) Gold colloid	Particle Size (nm) Gold powder	10^4 x k_{ss} (min^{-1})	Log k_{ss} versus log r
16		79	Nearly linear
25		47	
30		39	
	2250	3.5	
	7250	2.3	

[Cu(II)] = 1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120mM, pH 9.5 at 25 °C.

APPENDIX A4 Graphs of Results

Appendix A 4.1

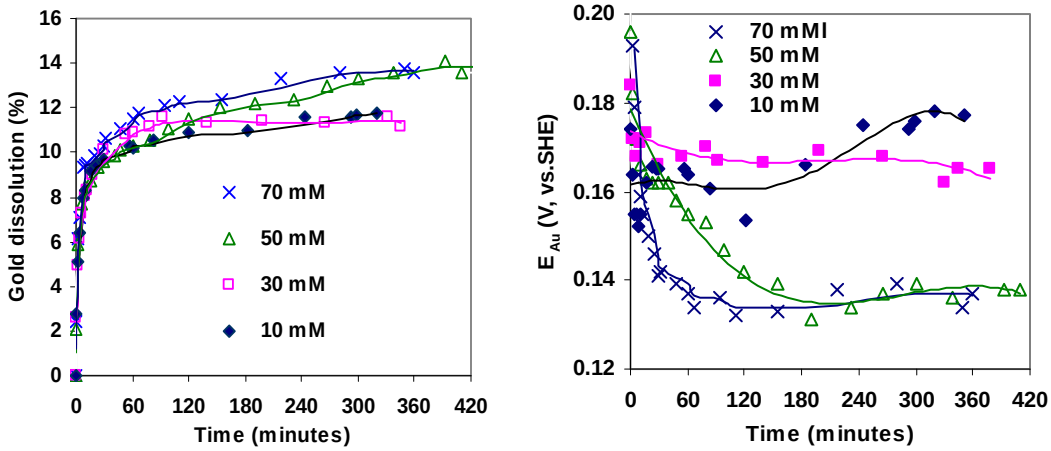


Fig. A4.1a *Effect of thiosulfate on gold dissolution in the absence of ammonia.*

Fig. A4.1b *Effect of thiosulfate on gold electrode potential in the absence of ammonia.*

pH = 9.3, I = 0.21, [O_2] = 0.25 mM.

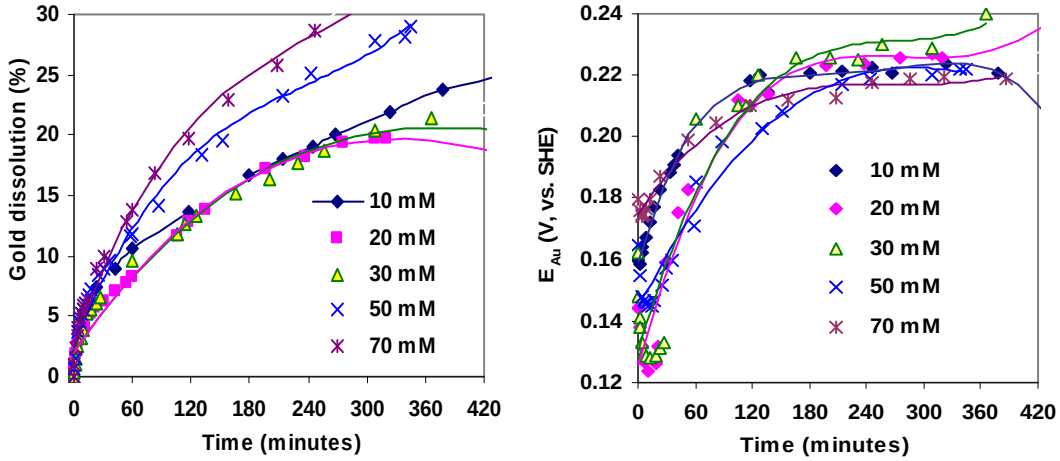


Fig. A4.1c *Effect of thiosulfate on gold dissolution in the presence of ammonia.*

Fig. A4.1d *Effect of thiosulfate on gold electrode potential in the presence of ammonia.*

[NH_3+NH_4^+] = 200 mM, pH = 9.5, [O_2] = 0.25 mM.

Appendix A 4.2

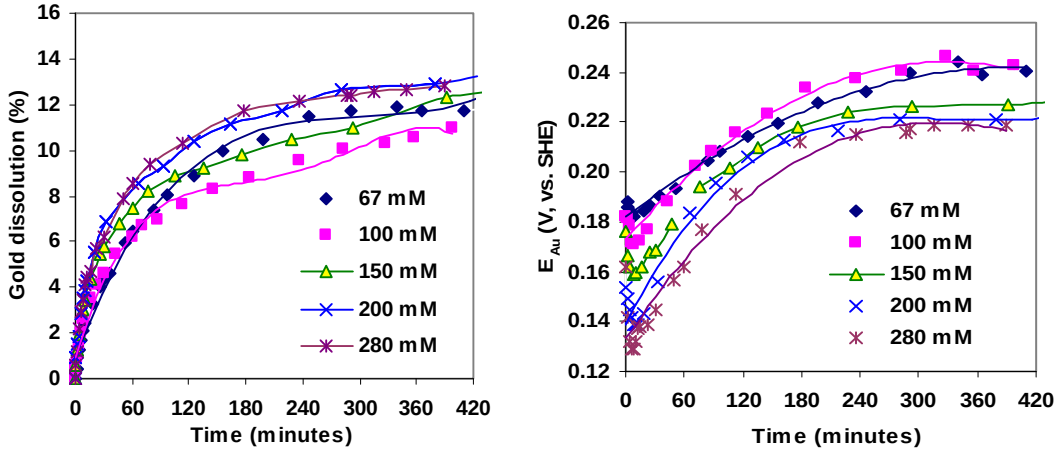


Fig. A4.2a *Effect of ammonia on gold dissolution in the absence of thiosulfate.*

Fig. A4.2b *Effect of ammonia on gold electrode potential in the absence of thiosulfate.*

pH = 9.5, I = 0.2 (Na_2SO_4), [O_2] = 0.25 mM.

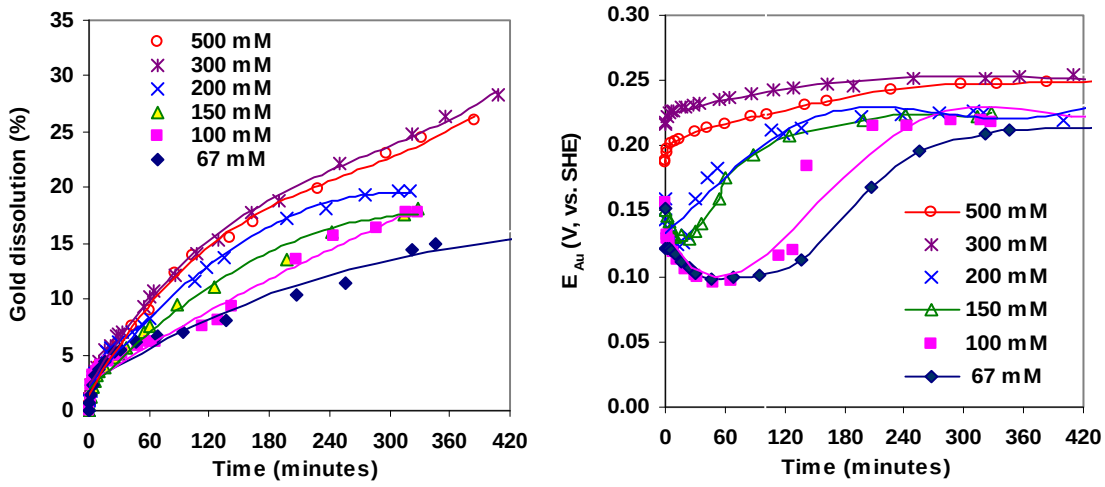


Fig. A4.2c *Effect of ammonia on gold dissolution in the presence of thiosulfate.*

Fig. A4.2d *Effect of ammonia on gold electrode potential in the presence of thiosulfate.*

[$Na_2S_2O_3$] = 20 mM, pH = 9.5, [O_2] = 0.25 mM.

Appendix A 4.3

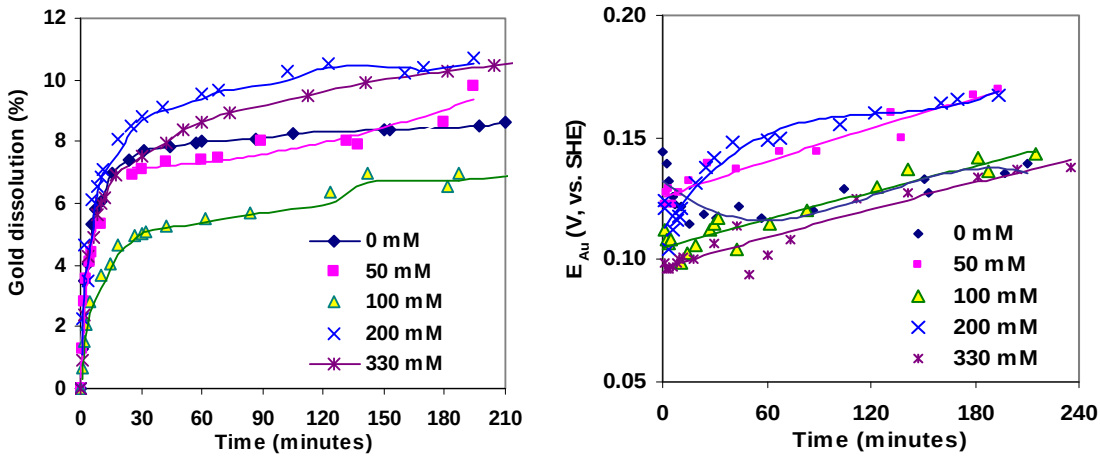


Fig. A4.3a *Effect of chloride on gold dissolution in the absence of ammonia.*

Fig. A4.3b *Effect of chloride on gold electrode potential in the absence of ammonia.*

[$Na_2S_2O_3$] = 30 mM, pH = 9.5, [O_2] = 0.25mM.

Appendix A 4.4

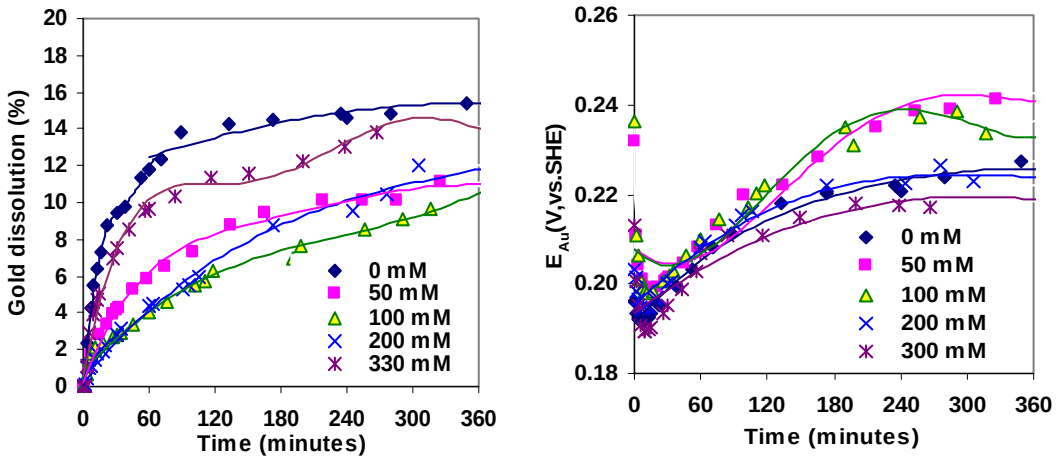


Fig. A4.4a *Effect of chloride on gold dissolution in the absence of thiosulfate.*

Fig. A4.4b *Effect of chloride on gold electrode potential in the absence of thiosulfate.*

[$Na_2S_2O_3$] = 0 mM, [NH_3+ NH_4^+] = 120 mM, pH = 9.5, [O_2] = 0.25 mM.

Appendix A 4.5

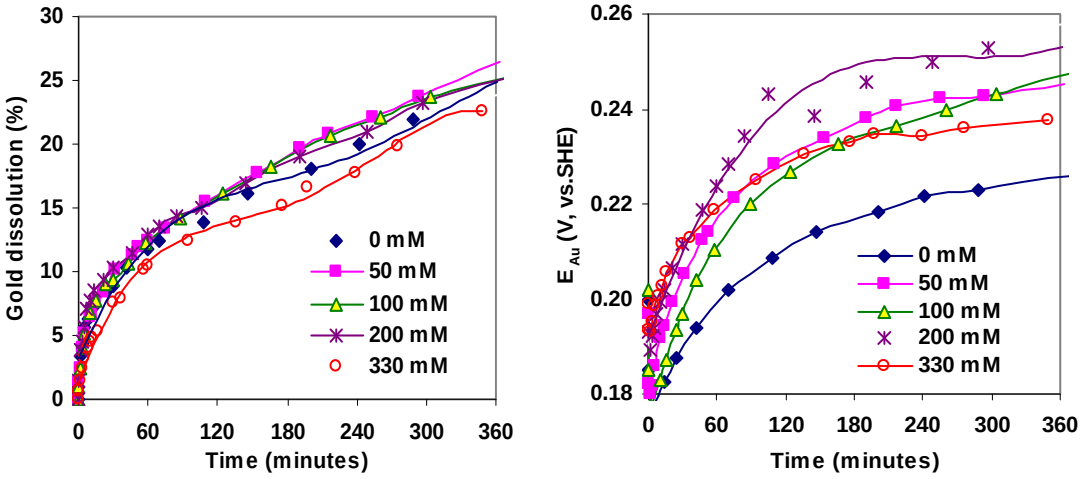


Fig. A4.5a *Effect of chloride on gold dissolution in the presence of both ammonia and thiosulfate.*

Fig. A4.5b *Effect of chloride on gold electrode potential in the presence of both ammonia and thiosulfate.*

[$Na_2S_2O_3$] = 20 mM, [NH_3+ NH_4^+] = 120 mM, pH = 9.5, [O_2] = 0.25 mM.

Appendix A 4.6

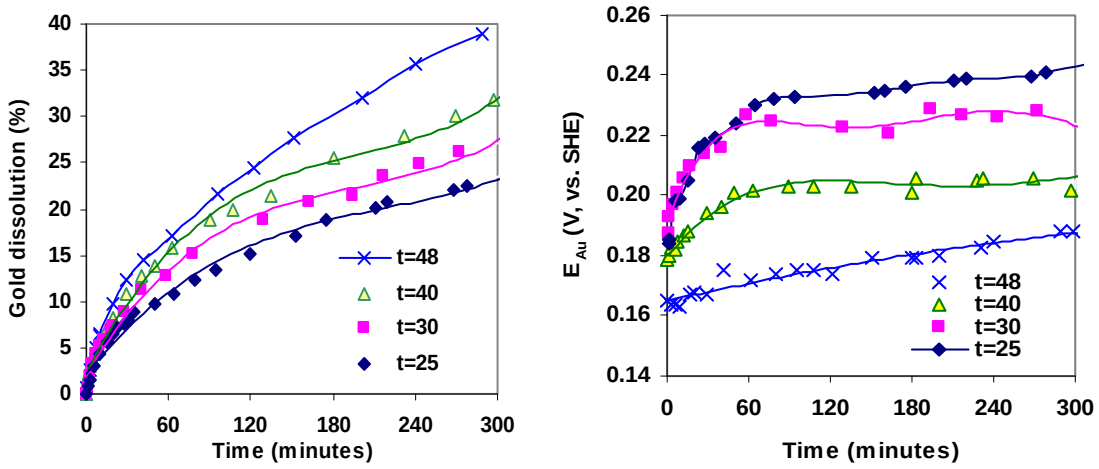
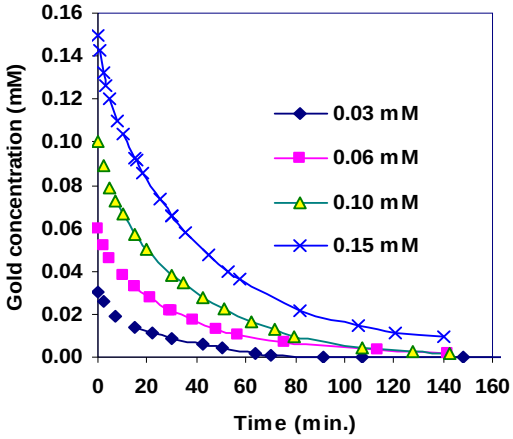


Fig. A4.6a *Effect of temperature on gold dissolution in oxygenated ammonia-thiosulfate solution.*

Fig. A4.6b *Effect of temperature on gold electrode potential in oxygenated ammonia-thiosulfate solution.*

[$Na_2S_2O_3$] = 20 mM, [NH_3+ NH_4^+] = 120 mM, pH = 9.5, [O_2] = 0.56 mM.

Appendix A 4.7



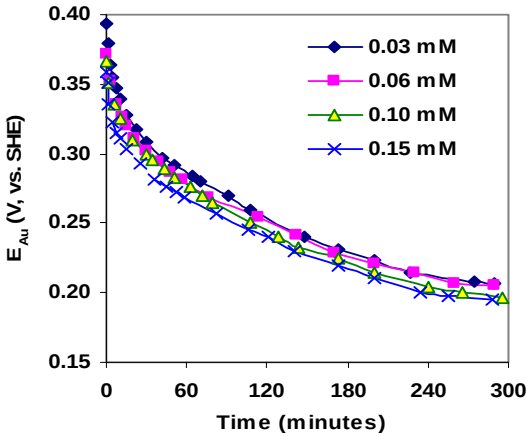


Fig. A4.7a *Effect of concentration of gold colloid on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.7b *Effect of concentration of gold colloid on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*

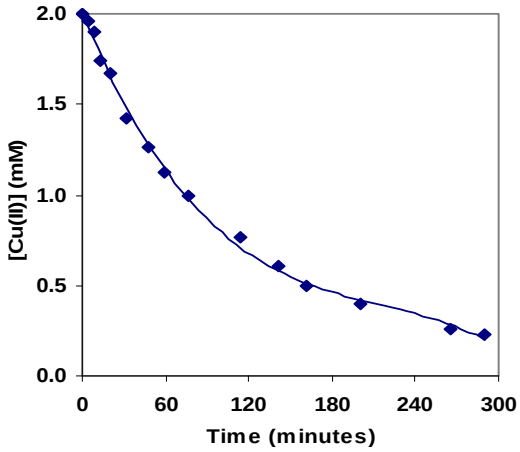


Fig. A4.7c *Change in residual concentration of copper(II) in copper(II)-ammonia-thiosulfate solution.*
[$CuSO_4$] = 2.0 mM, [$Na_2S_2O_3$] = 50 mM, [$NH_3 + NH_4^+$] = 240 mM, pH = 9.5.

Appendix A 4.8

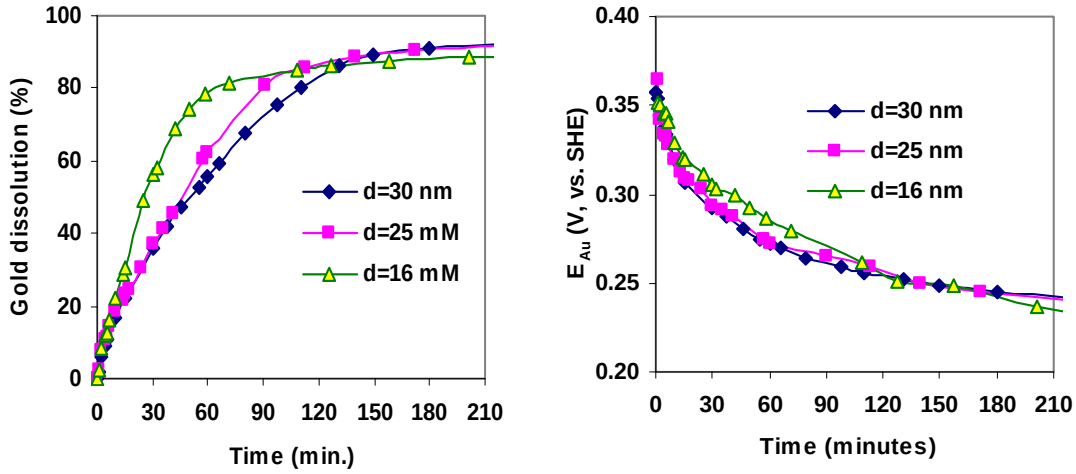


Fig. A4.8a *Effect of particle size of stabilized gold colloids on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.8b *Effect of particle size of stabilized gold colloids on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*
[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3 +NH_4^+] = 120 mM, pH = 9.5.

Appendix 4.9

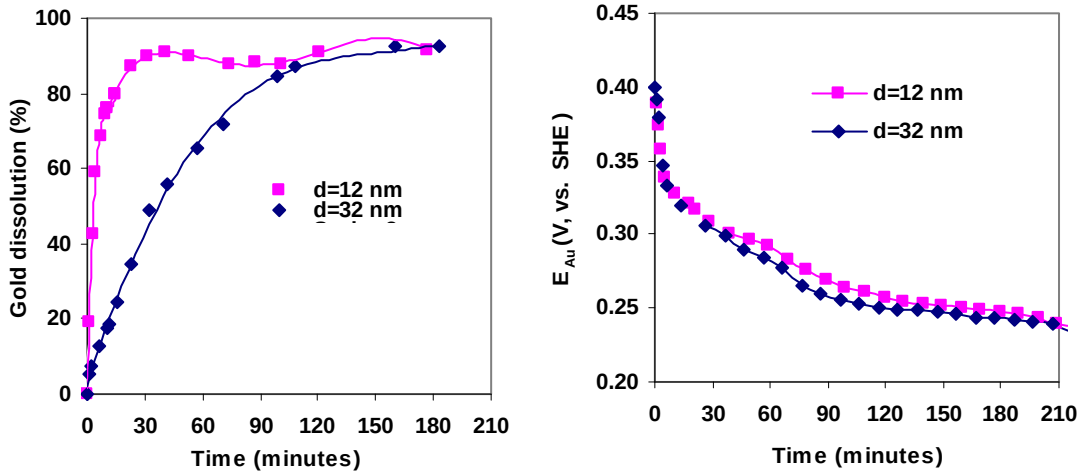


Fig. A4.9a *Effect of particle size of unstabilized gold colloid on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.9b *Effect of particle size of unstabilized gold colloid on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*
[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.10

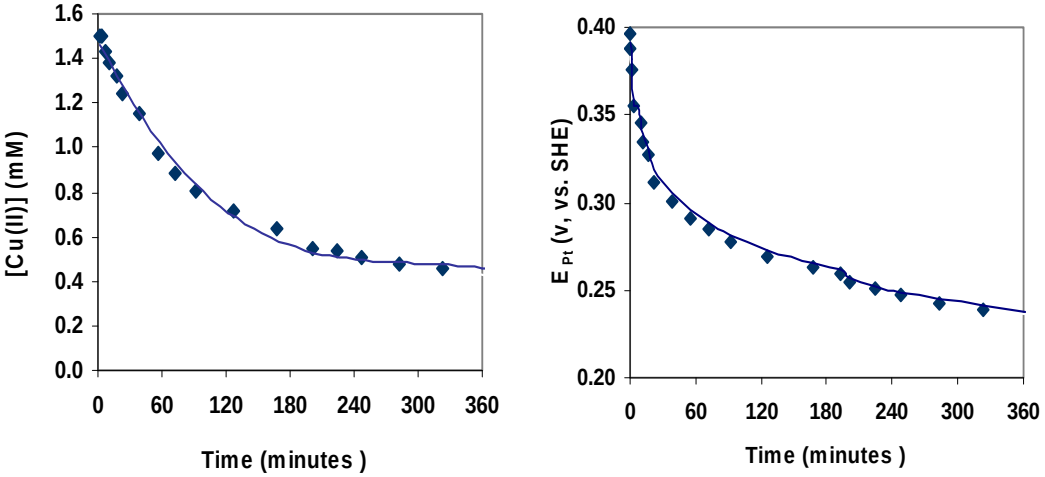


Fig. A4.10a *Copper(II) concentration during reaction of copper(II) and thiosulfate in copper(II)-ammonia-thiosulfate solution in the absence of gold colloids.*

Fig. A4.10b *Platinum electrode potential during reaction of copper(II) and thiosulfate in copper(II)-ammonia-thiosulfate solution in the absence of gold colloids.*
[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3 +NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.11

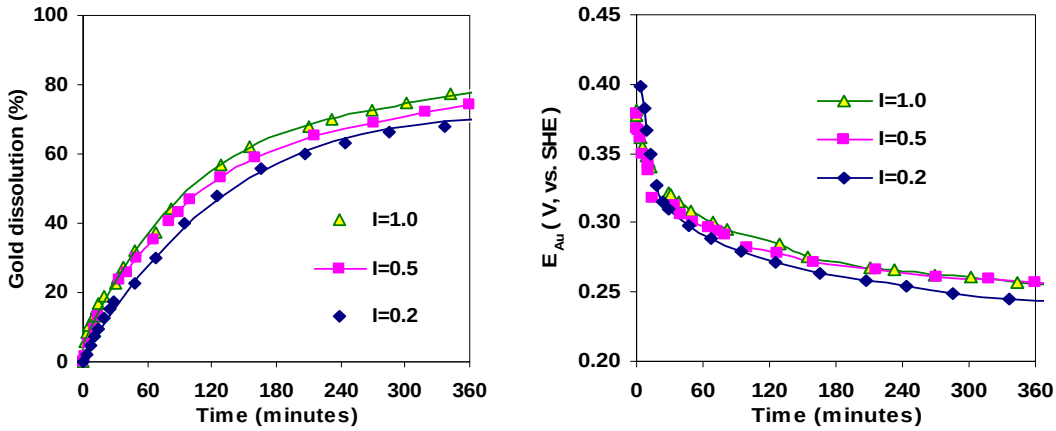


Fig. A4.11a *Effect of ionic strength on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.11b *Effect of ionic strength on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] =10 mM, [NH_3 +NH_4^+] = 60 mM, pH = 9.5.

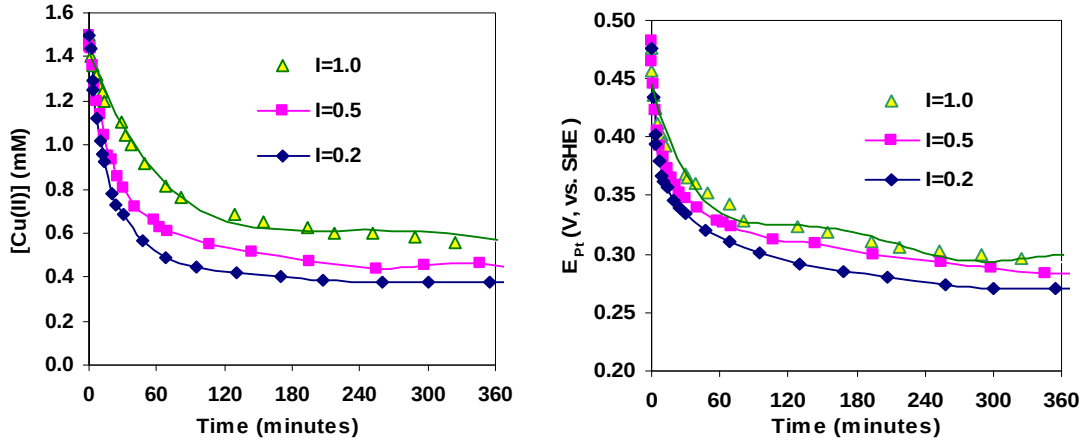


Fig. A4.11c *Effect of ionic strength on concentration of copper(II) in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.11d *Effect of ionic strength on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 10 mM, [NH_3 +NH_4^+] = 60 mM, pH = 9.5.

Appendix A 4.12

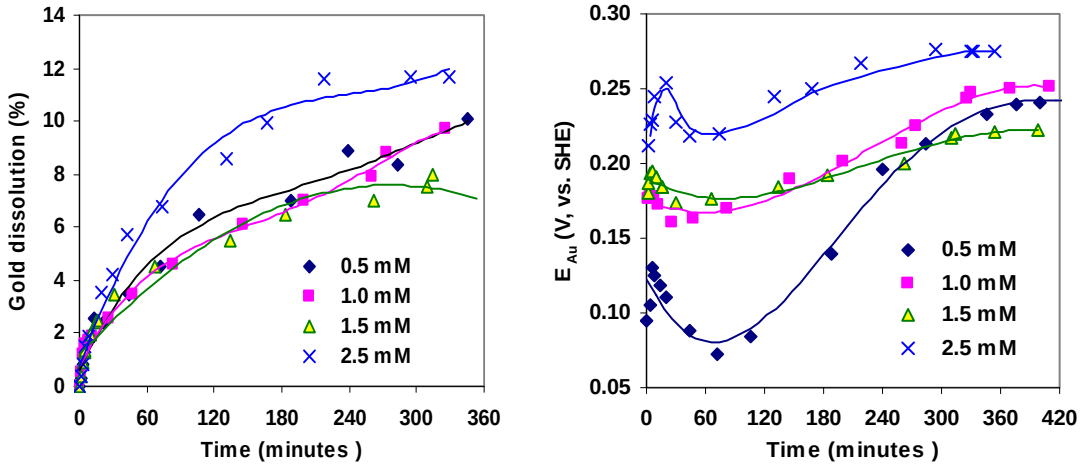
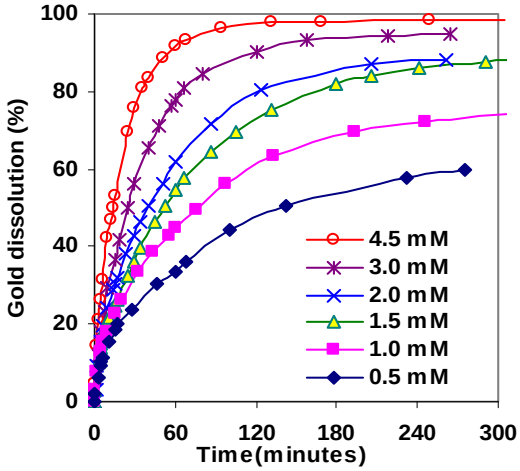


Fig. A4.12a *Effect of copper(II) on gold dissolution in the absence of thiosulfate.*

Fig. A4.12b *Effect of copper(II) on gold electrode potential in the absence of thiosulfate.*

$[Na_2S_2O_3]$ = 0 mM, $[NH_3 + NH_4^+]$ = 120 mM, pH = 9.5.

Appendix A 4.13



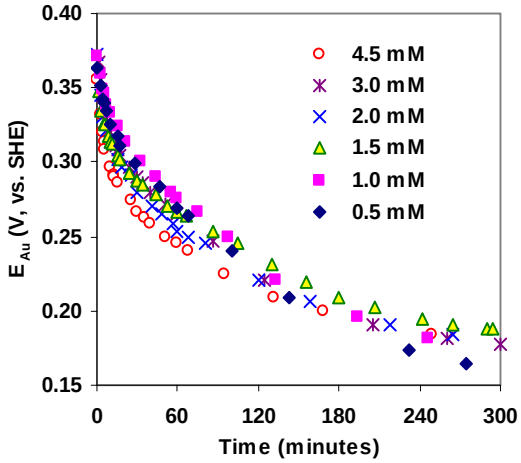
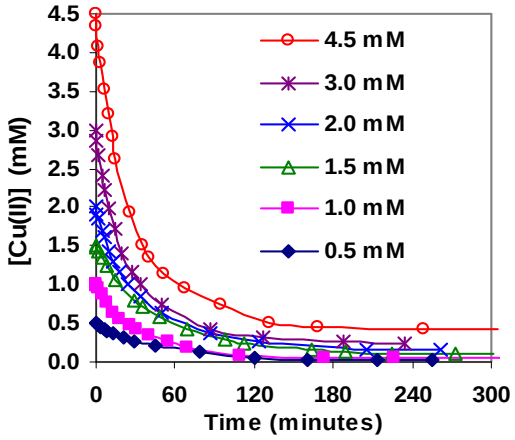


Fig. A4.13a *Effect of copper(II) on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.13b *Effect of copper(II) on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.



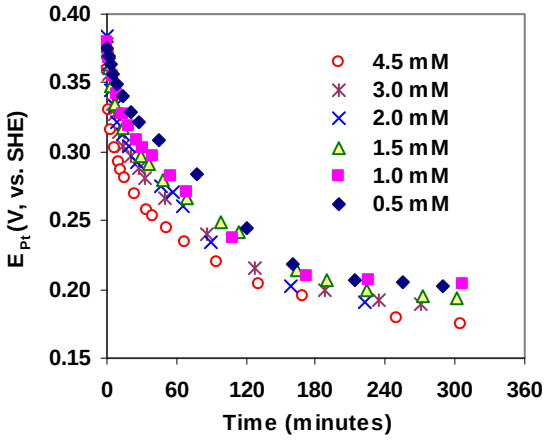


Fig. A4.13c *Effect of initial copper(II) concentration on residual copper(II) in copper(II)-ammonia-thiosulfate solution*

Fig. A4.13d *Effect of copper(II) on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3.

Appendix A 4.14

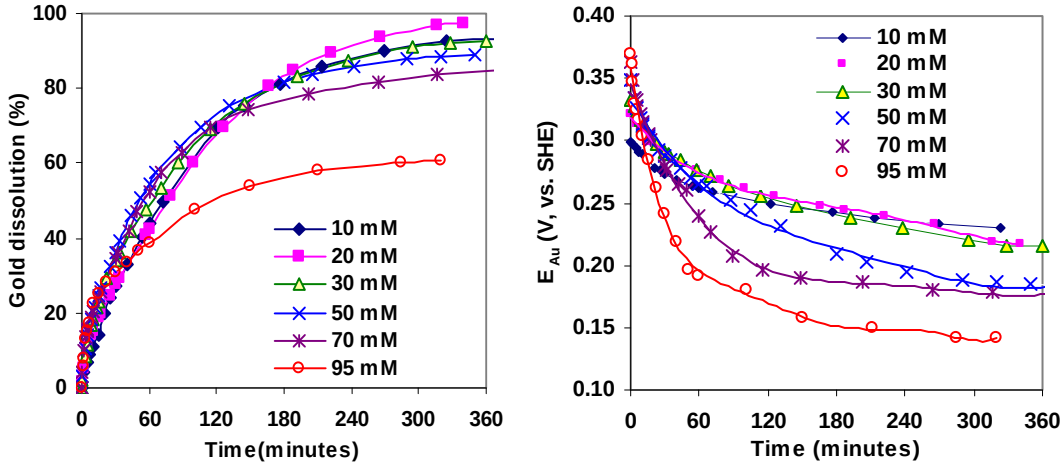


Fig. A4.14a *Effect of thiosulfate on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.14b *Effect of thiosulfate on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

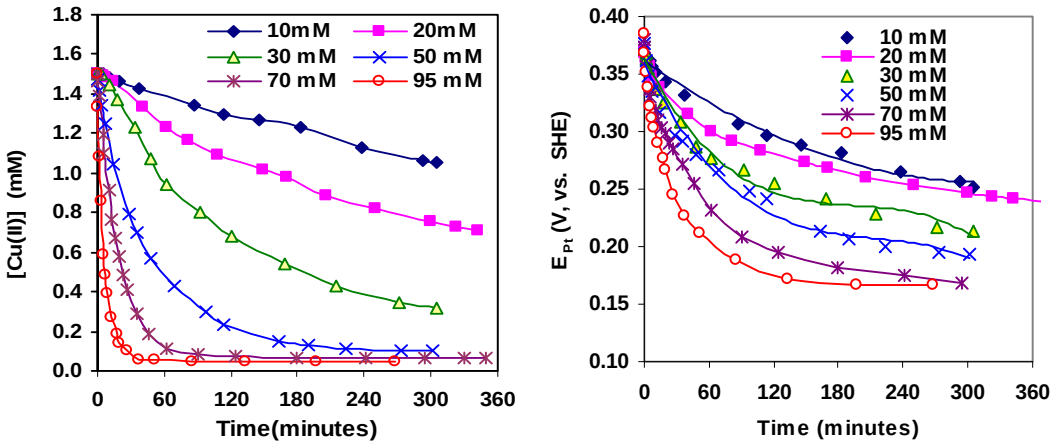


Fig. A4.14c *Effect of thiosulfate on copper(II) concentration in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.14d *Effect of thiosulfate on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[Cu(II)] = 1.5 mM, [NH_3 +NH_4^+] = 240 mM, pH = 9.3.

Appendix A 4.15

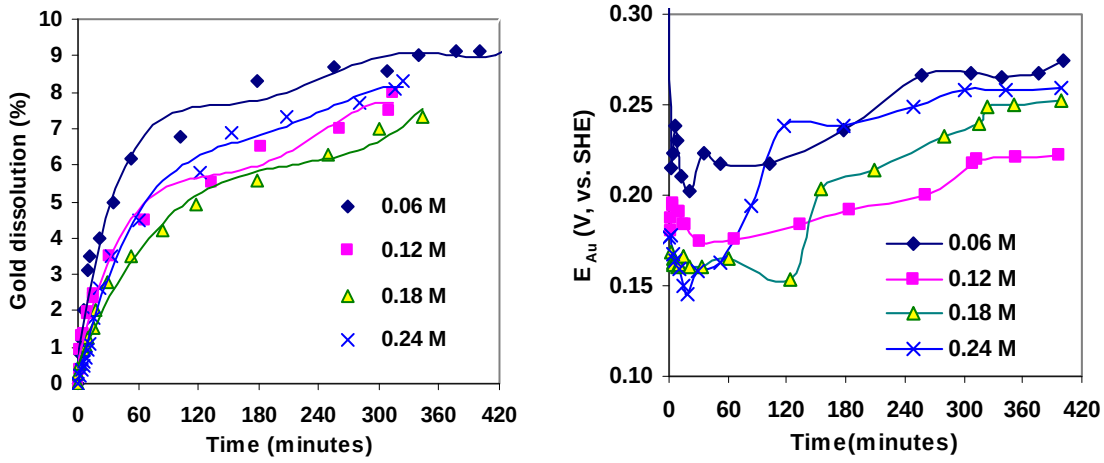


Fig. A4.15a *Effect of ammonia on gold dissolution in the absence of thiosulfate.*

Fig. A4.15b *Effect of ammonia on gold electrode potential in the absence of thiosulfate.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 0 mM, pH = 9.5.

Appendix A 4.16

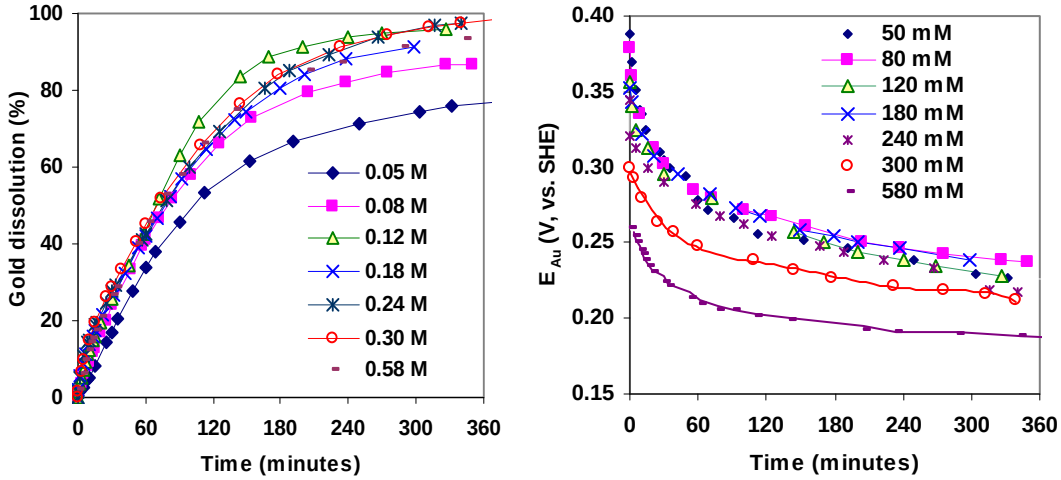


Fig. A4.16a *Effect of ammonia on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.16b *Effect of ammonia on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*

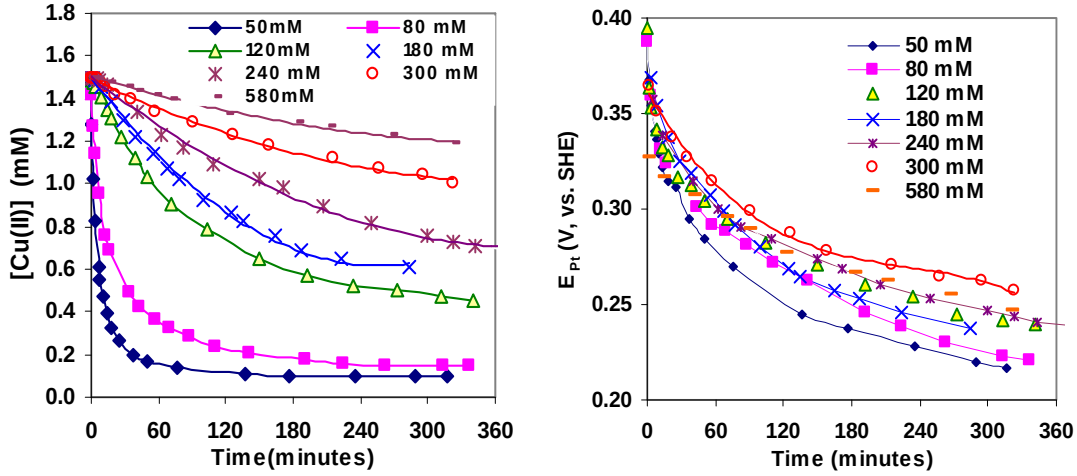


Fig. A4.16c *Effect of ammonia on copper(II) concentration in copper(II)-ammonia-thiosulfate solution .*

Fig. A4.16d *Effect of ammonia on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, pH = 9.3.

Appendix A 4.17

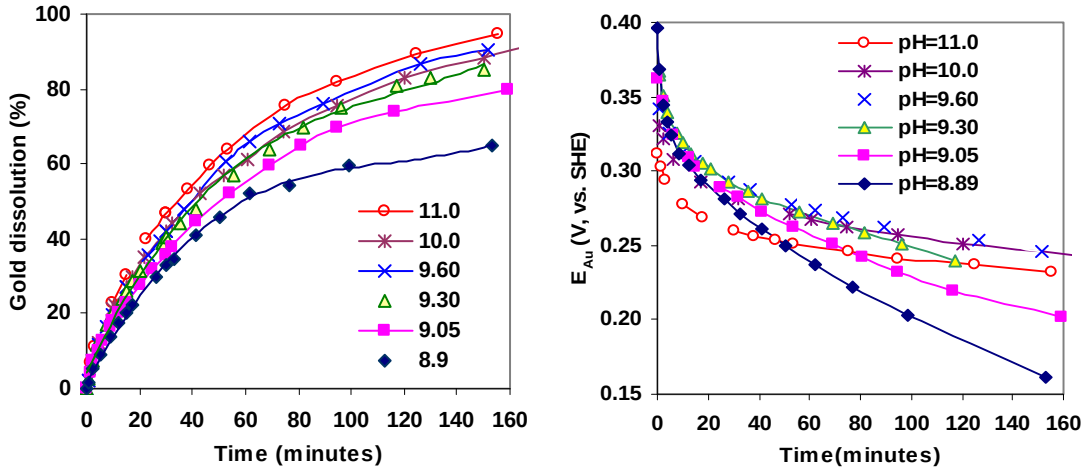


Fig. A4.17a *Effect of pH on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.17b *Effect of pH on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*

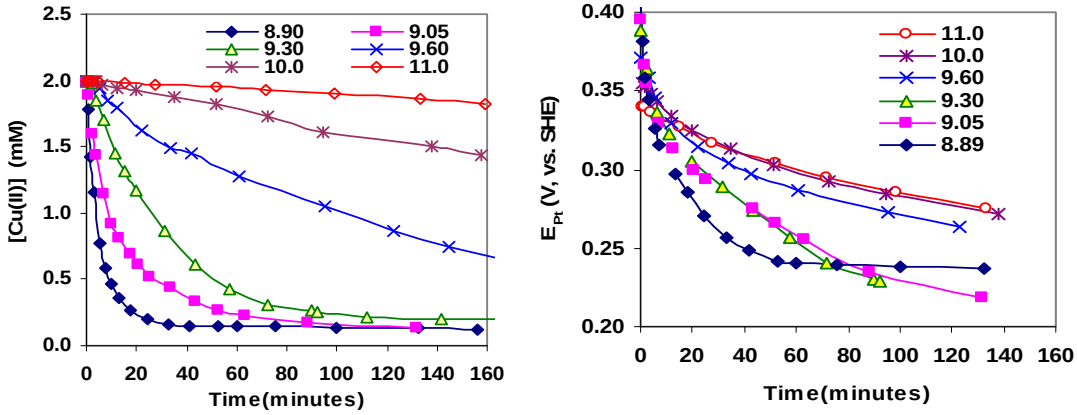


Fig. A4.17c *Effect of pH on copper(II) concentration in copper(II)-ammonia thiosulfate solution .*

Fig. A4.17d *Effect of pH on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 2.0 mM, [$Na_2S_2O_3$] = 40 mM, [NH_3+NH_4^+] = 240 mM.

Appendix A 4.18

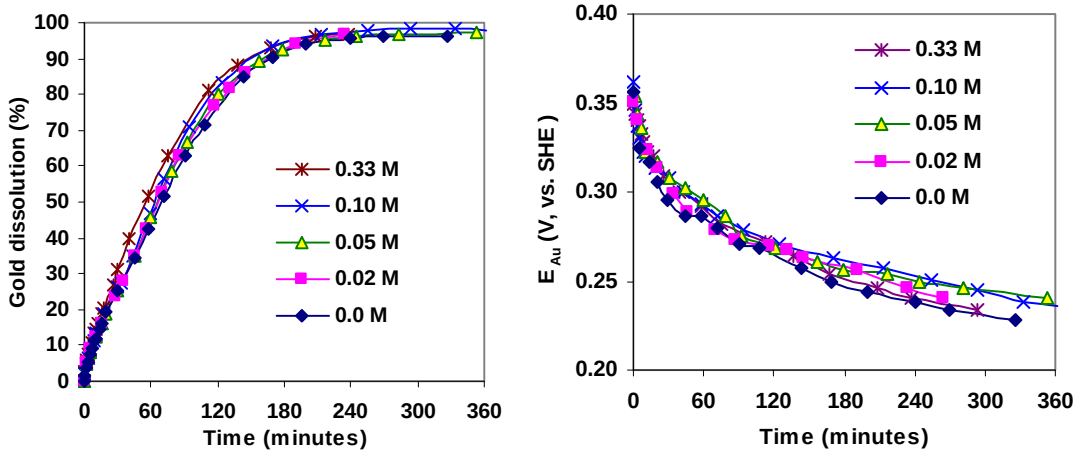


Fig. A4.18a *Effect of nitrate on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.18b *Effect of nitrate on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

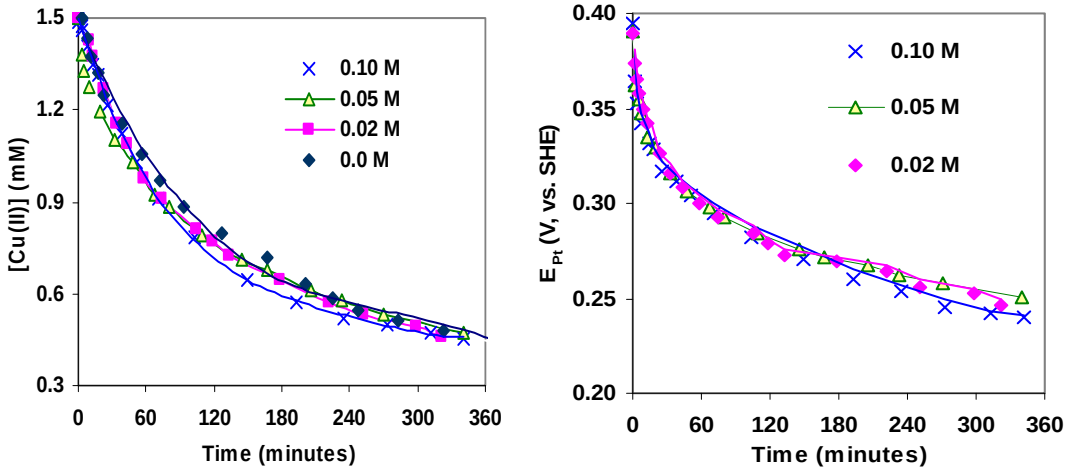


Fig. A4.18c *Effect of nitrate on copper(II) concentration in copper(II)-ammonia-thiosulfate solution .*

Fig. A4.18d *Effect of nitrate on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.19

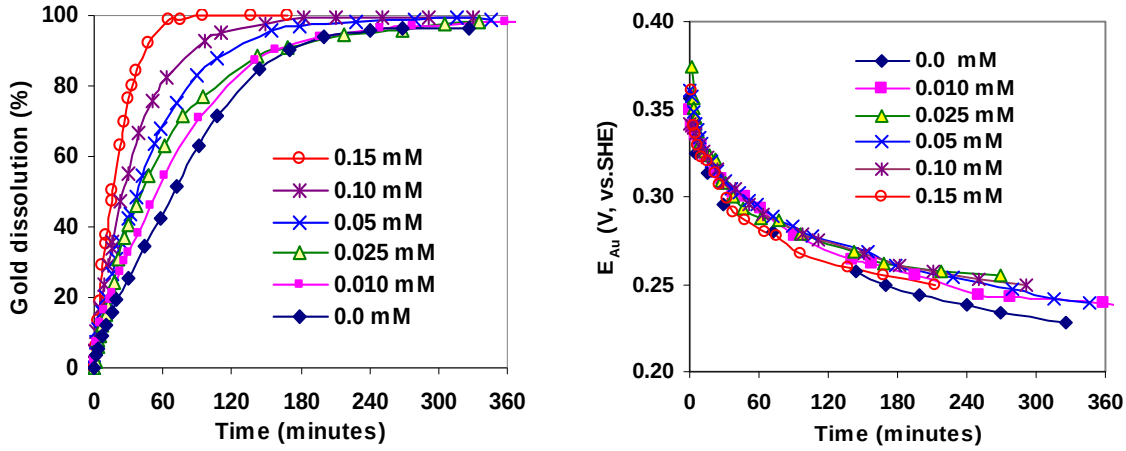


Fig. A4.19a *Effect of silver(I) on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.19b *Effect of silver(I) on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

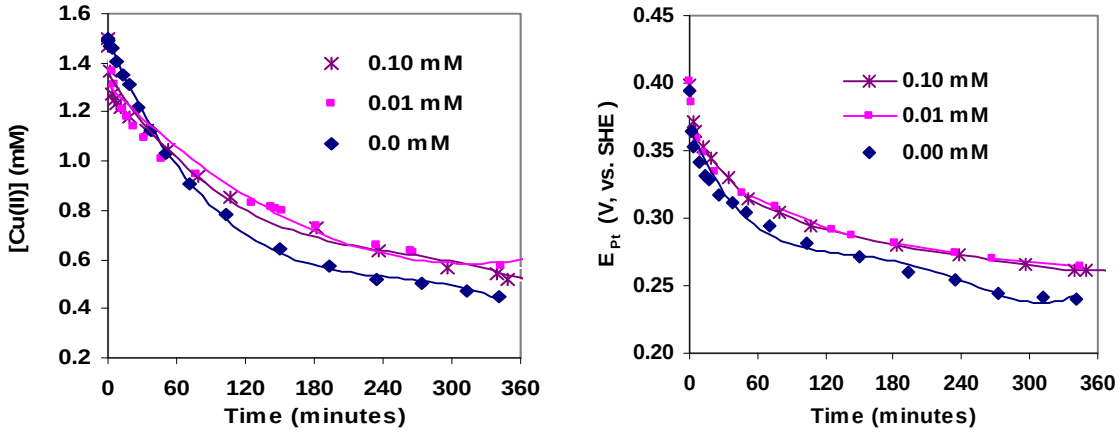


Fig. A4.19c *Effect of silver(I) on copper(II) concentration in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.19d *Effect of silver(I) on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.20

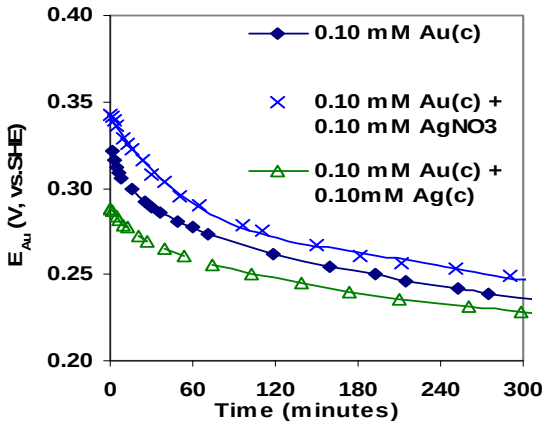


Fig. A4.20a *Comparison of gold electrode potentials in the presence of silver colloid or silver nitrate.*

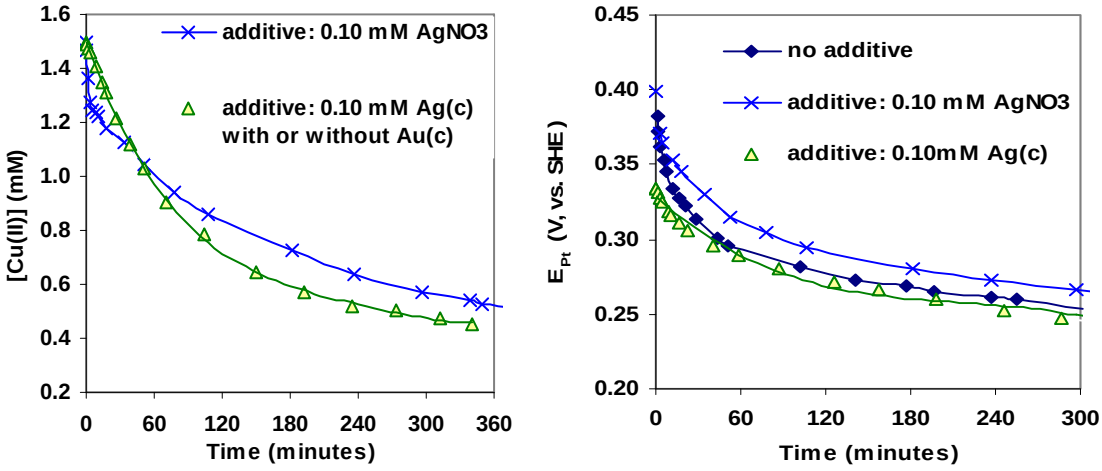


Fig. A4.20b *Copper concentrations in the presence of silver colloid or silver nitrate.*

Fig. A4.20c *Platinum electrode potential in the presence of silver colloid or silver nitrate.*

[Cu(II)] = 1.5 mM, [NH_3+NH_4^+] = 120 mM, [$Na_2S_2O_3$] = 20 mM, [Ag(c)] = 0.1 mM, pH = 9.5.

Appendix A 4.21

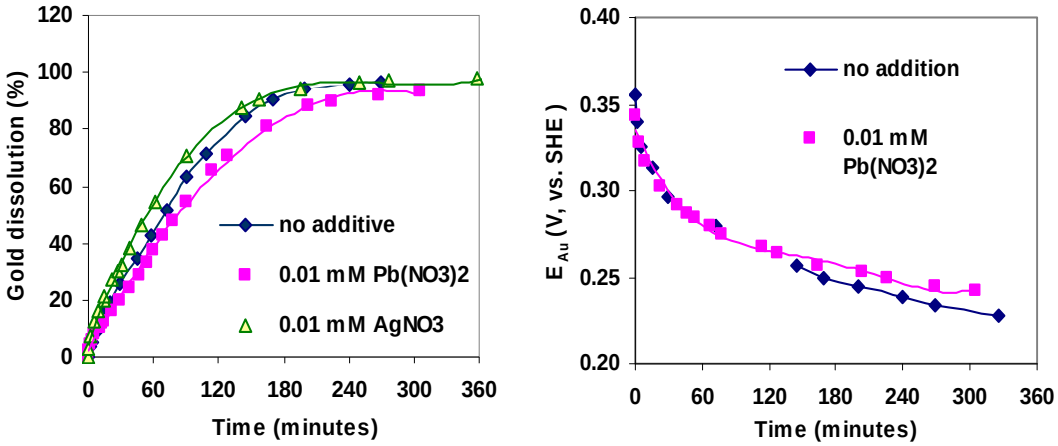


Fig. A4.21a *Comparison of gold dissolution in the presence of lead(II) or silver nitrate.*

Fig. A4.21b *Gold electrode potential in the presence of lead(II).*

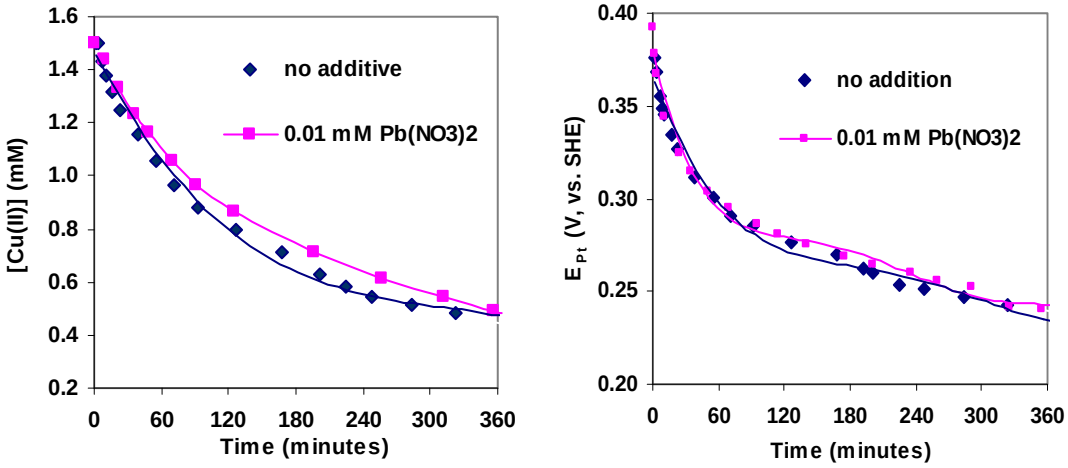


Fig. A4.21c *Copper(II) concentration in the present of lead(II).*

Fig. A4.21d *Platinum electrode potential in the present of lead(II).*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.22

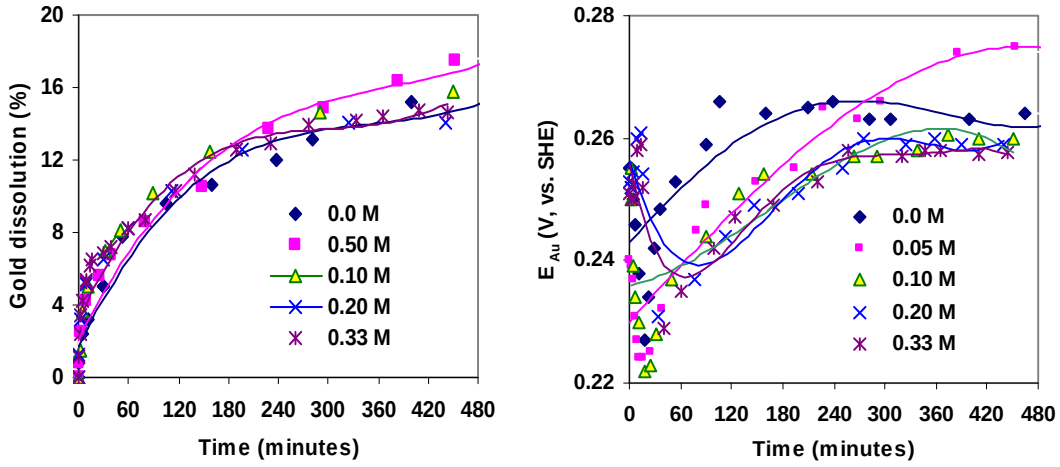


Fig. A4.22a *Effect of chloride on gold dissolution in the absence of thiosulfate.*

Fig. A4.22b *Effect of chloride on gold electrode potential in the absence of thiosulfate.*

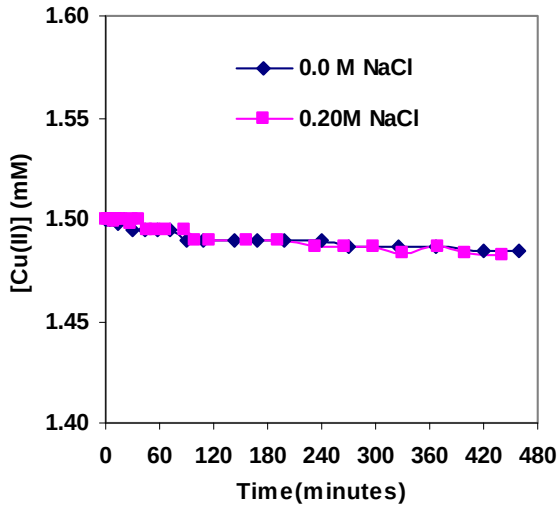


Fig. A4.22c *Effect of chloride on copper(II) concentration in the absence of thiosulfate.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 0 mM, [NH_3+NH_4^+] = 200 mM, pH = 9.5.

Appendix A 4.23

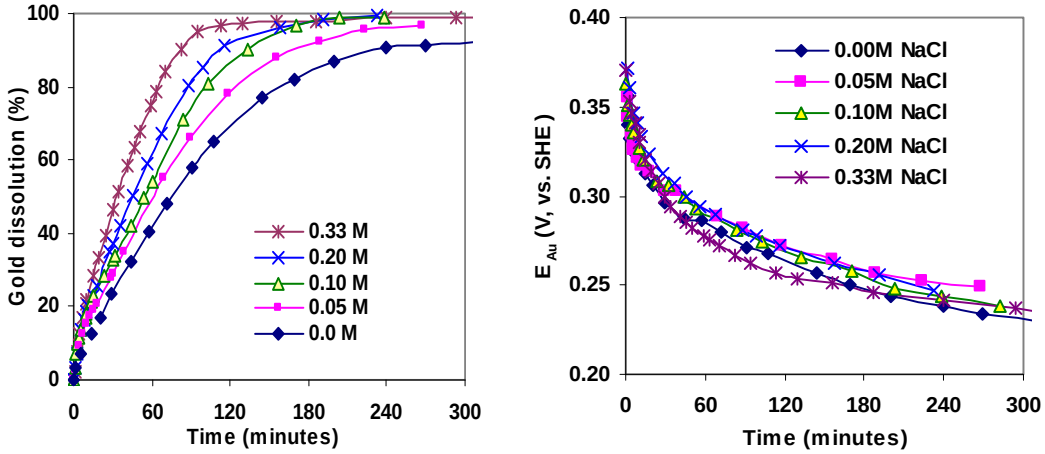


Fig. A4.23a *Effect of chloride on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.23b *Effect of chloride on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

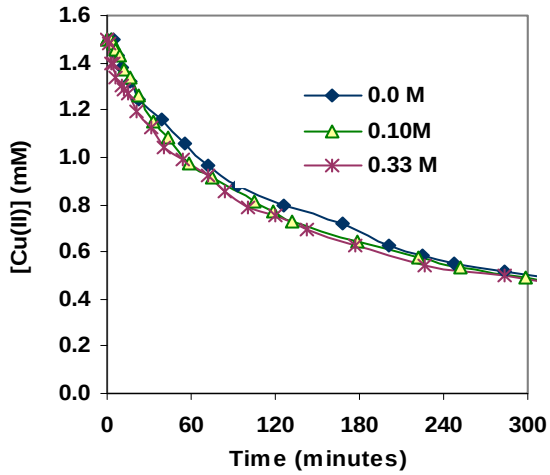


Fig. A4.23c *Effect of chloride on copper(II) concentration in copper(II)-ammonia-thiosulfate solution .*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.24

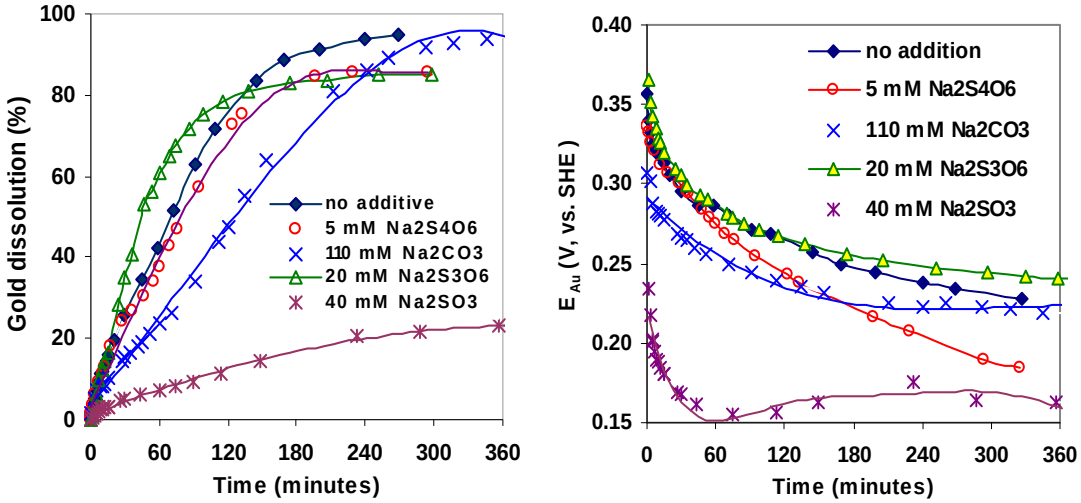


Fig. A4.24a *Effect of $S_3O_6^{2-}$, $S_4O_6^{2-}$, CO_3^{2-} and SO_3^{2-} on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.24b *Effect of $S_3O_6^{2-}$, $S_4O_6^{2-}$, CO_3^{2-} and SO_3^{2-} on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

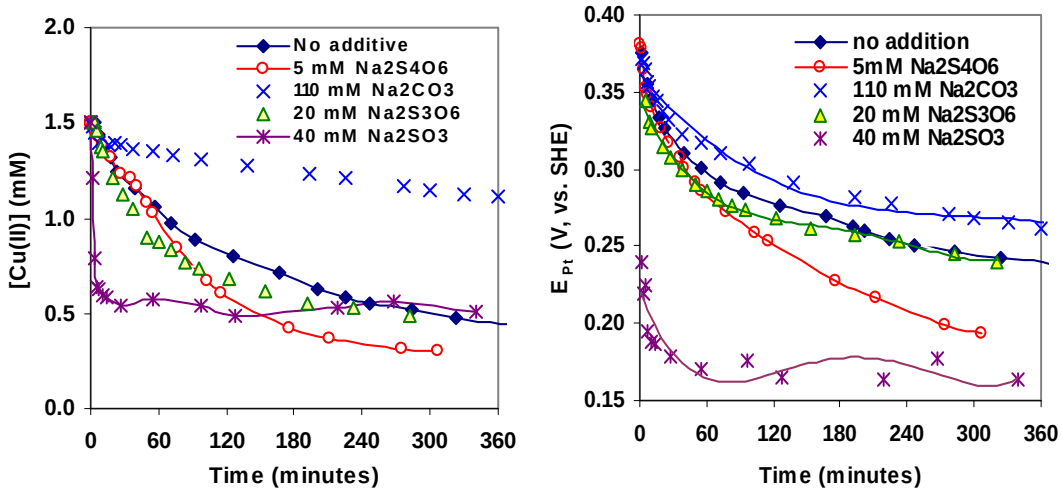


Fig. A4.24c *Effect of $S_3O_6^{2-}$, $S_4O_6^{2-}$, CO_3^{2-} and SO_3^{2-} on copper(II) concentration in copper(II)-ammonia-thiosulfate solution .*

Fig. A4.24d *Effect of $S_3O_6^{2-}$, $S_4O_6^{2-}$, CO_3^{2-} and SO_3^{2-} on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

$[CuSO_4]$ = 1.5 mM, $[Na_2S_2O_3]$ = 20 mM, $[NH_3+NH_4^+]$ = 120 mM, pH = 9.5.

Appendix A 4.25

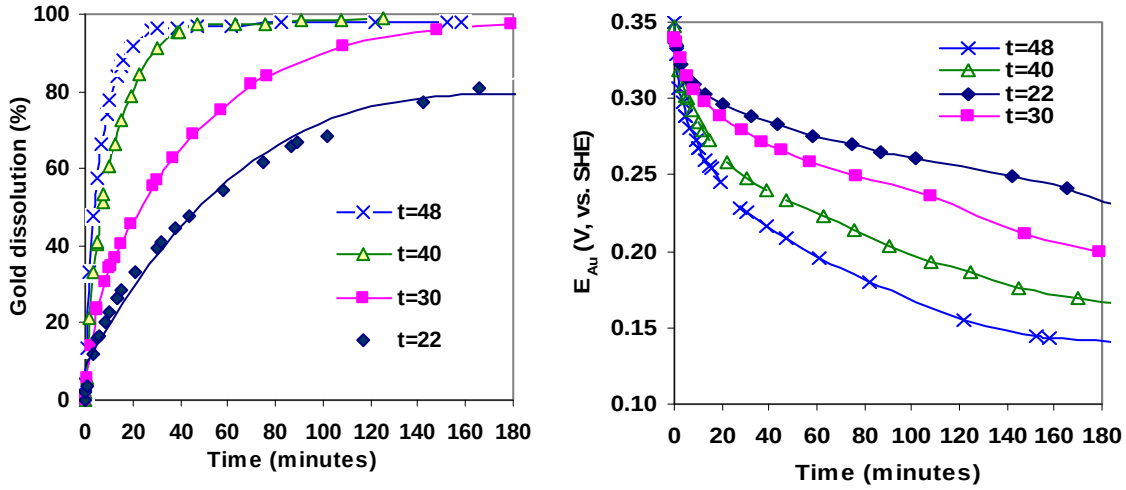


Fig. A4.25a *Effect of temperature on gold dissolution in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.25b *Effect of temperature on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

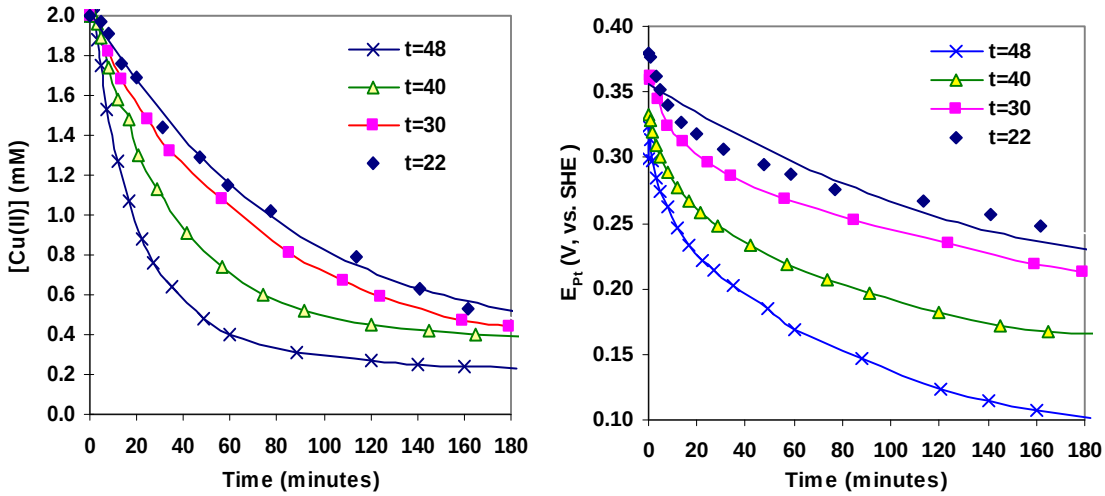


Fig. A4.25c *Effect of temperature on copper(II) concentration in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.25d *Effect of temperature on platinum electrode potential in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 2 mM, [$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.5.

Appendix A 4.26

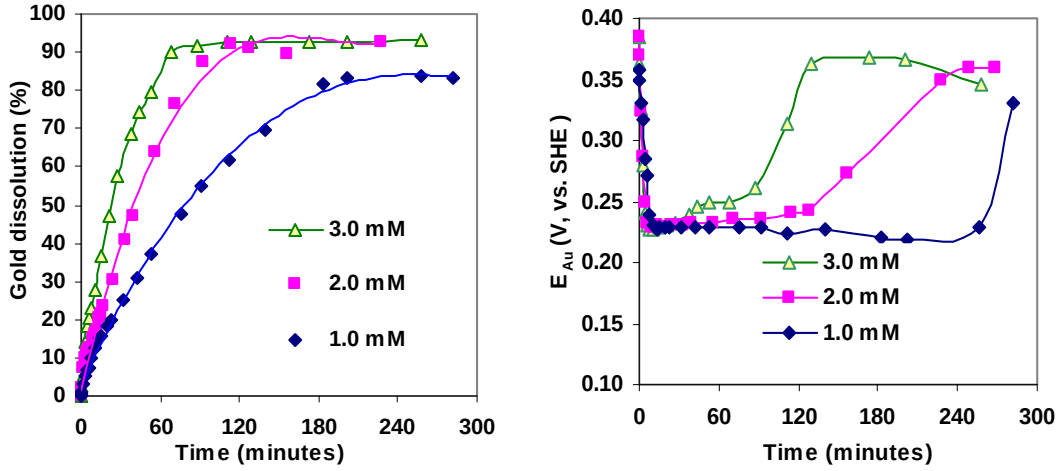


Fig. A4.26a *Effect of copper(II) on gold dissolution in oxygenated copper(II)-ammonia-thiosulfate solution.*

Fig. A4.26b *Effect of copper(II) on gold electrode potential in oxygenated copper(II)-ammonia-thiosulfate solution.*

[$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3, [O_2] = 0.31 mM.

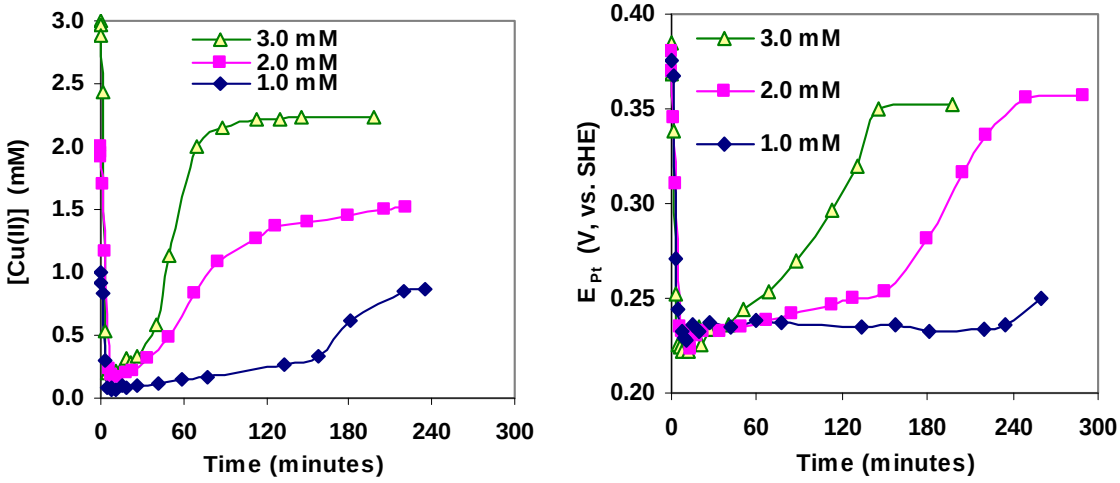


Fig. A4.26c *Variation of copper(II) concentration in oxygenated copper(II)-ammonia-thiosulfate solution .*

Fig. A4.26d *Effect of copper(II) on platinum electrode potential in oxygenated copper(II)-ammonia-thiosulfate solution.*

[$Na_2S_2O_3$] = 50 mM, [NH_3+NH_4^+] = 240 mM, pH = 9.3, [O_2] = 0.31 mM.

Appendix A 4.27

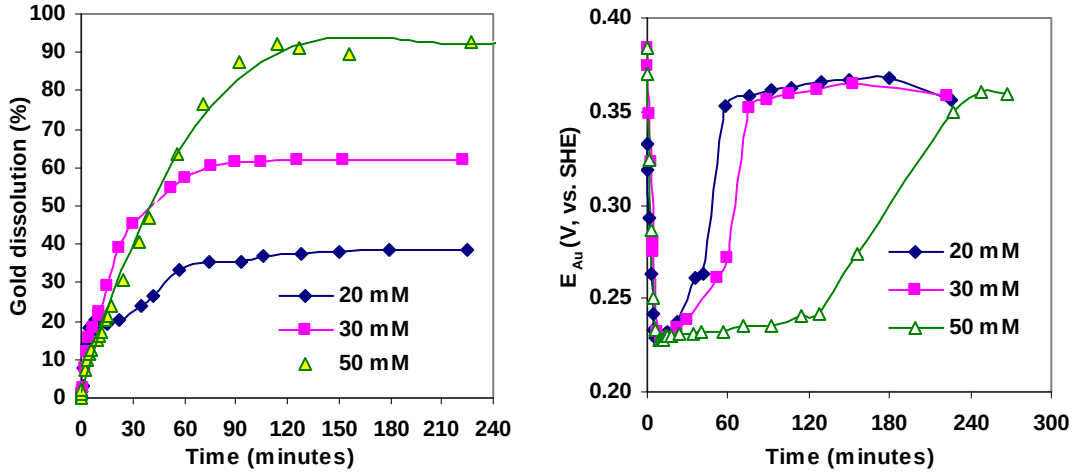


Fig. A4.27a *Effect of thiosulfate on gold dissolution in oxygenated copper(II)-ammonia-thiosulfate solution.*

Fig. A4.27b *Effect of thiosulfate on gold electrode potential in oxygenated copper(II)-ammonia-thiosulfate solution*.

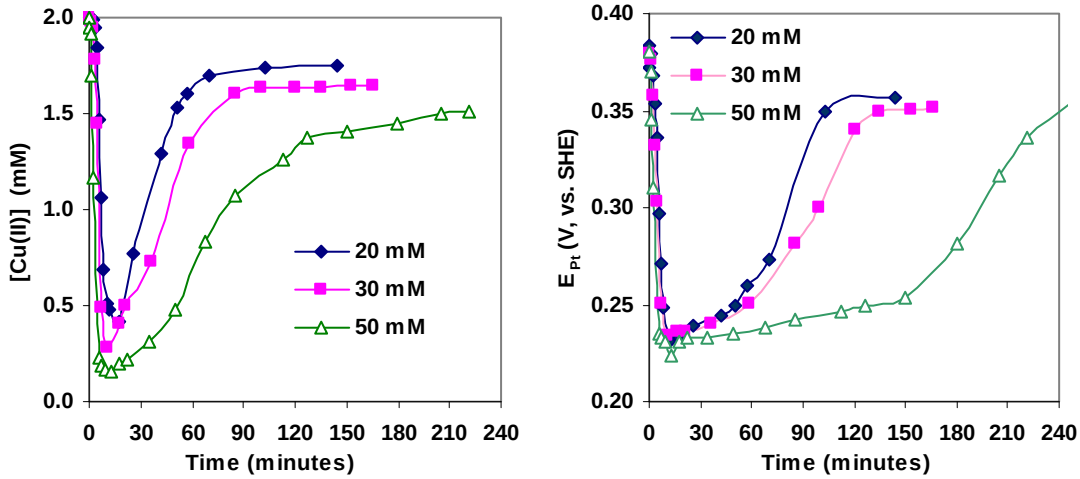


Fig. A4.27c *Effect of thiosulfate on copper(II) concentration in oxygenated copper(II)-ammonia-thiosulfate solution*

Fig. A4.27d *Effect of thiosulfate on platinum electrode potential in oxygenated copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 2.0 mM, [NH_3+NH_4^+] = 240 mM, [O_2] = 0.31 mM, pH = 9.3.

Appendix A 4.28

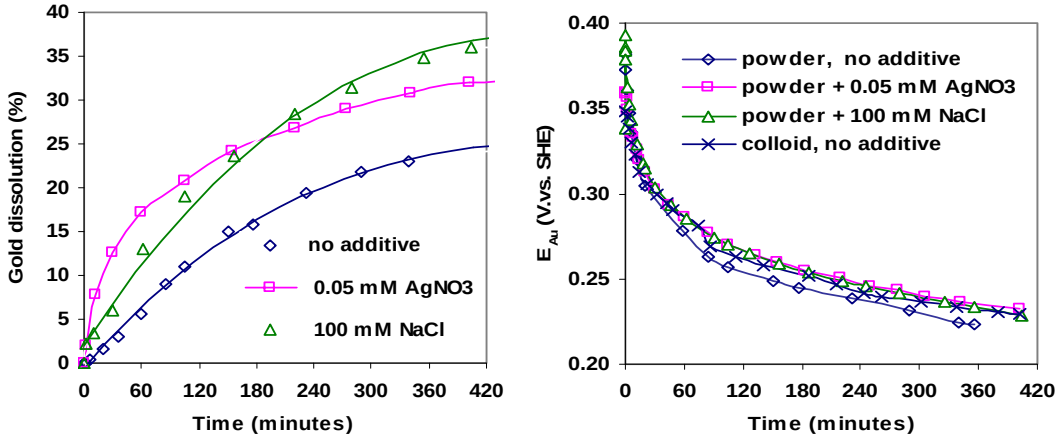


Fig. A4.28a *Effect of silver(I) and chloride ions on the dissolution of gold powder in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.28b *Effect of silver(I) and chloride ions on gold electrode potential in copper(II)-ammonia-thiosulfate solution.*

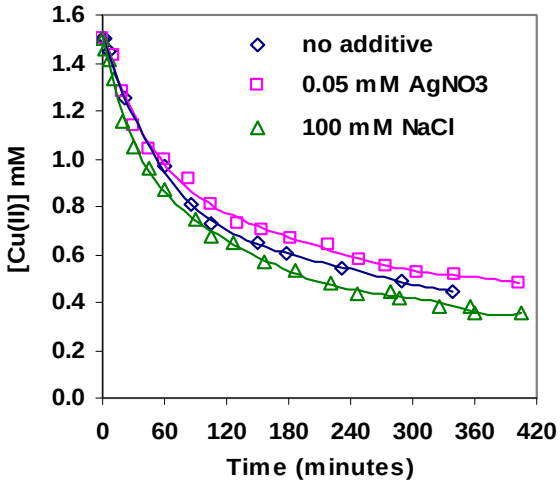


Fig. A4.28c *Effect of silver(I) and chloride ions on copper(II) concentration in copper(II)-ammonia-thiosulfate solution.*
Gold powder particle size: 1.5 µm - 3.0 µm.
[$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

Appendix A 4.29

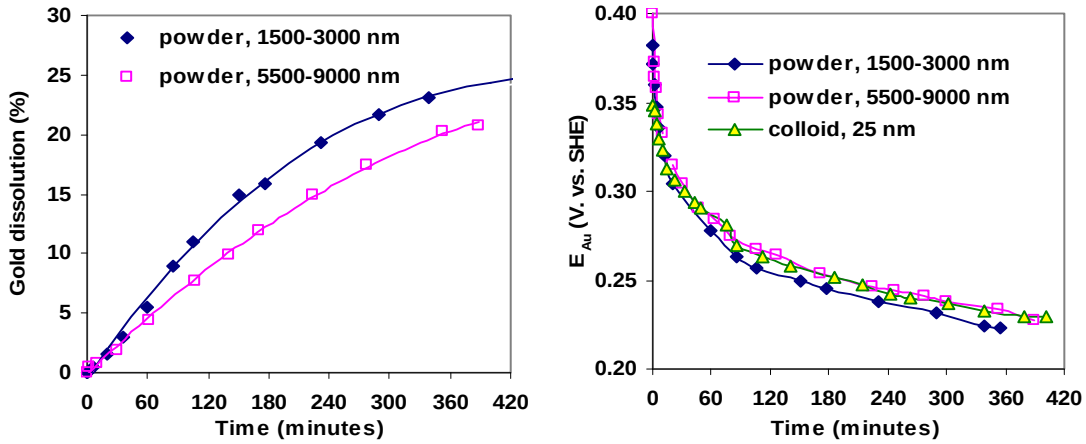


Fig. A4.29a *Dissolution of gold powder with difference particle size in copper(II)-ammonia-thiosulfate solution.*

Fig. A4.29b *Effect of particle size of gold powder on gold electrode potential in copper(II)-ammonia-thiosulfate solution*.

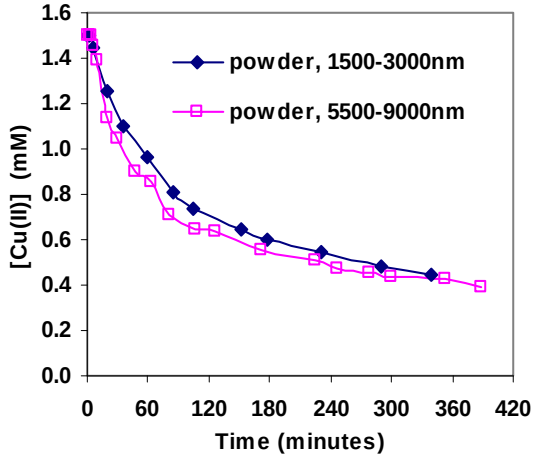


Fig. A4.29c *Effect of particle size of gold powder on copper(II) concentration in copper(II)-ammonia-thiosulfate solution.*

[$CuSO_4$] = 1.5 mM, [$Na_2S_2O_3$] = 20 mM, [NH_3+NH_4^+] = 120 mM, pH = 9.5.

APPENDIX A5 Reaction order and electrochemistry theory

In Au(c)-Cu(II)-NH_3-S_2O_3-N_2 system, initial rates of gold dissolution show reaction orders of 0.41, 0.49 and 0.60 with respect to the concentrations of copper(II), thiosulfate, ammonia respectively. Principle reaction factors: copper (II), thiosulfate, ammonia, and pH all have near one-half order for reaction rate, this reasons can be explained by electrochemical theory.

Anodic half-cell reaction would be the oxidation reaction of gold in aqueous solution:

$$2Au + 2S_2O_3^{2-} + 2NH_3 \rightarrow Au(S_2O_3)_2^{3-} + Au(NH_3)^+_2 + 2e \quad (A1)$$

While the cathodic half-cell reaction would be the reduction of copper (II) to copper (I)

$$Cu(NH_3)_4^{2+} + e \rightarrow Cu(NH_3)_2^{+} + 2NH_3 \quad (A2)$$

The overall reaction is:

$$2Au + 2S_2O_3^{2-} + 2Cu(NH_3)_4^{2+} \rightarrow Au(S_2O_3)_2^{3-} + Au(NH_3)^+_2 + Cu(NH_3)_2^{+} + 2NH_3 \quad (A3)$$

According to the electrochemical model (Nicol and Lazaro, 2002), the rate of the two electrochemical reaction in Eqs. A1 and A2 can thus be represented by the anodic and cathodic currents i_a and i_c:

$$i_a = F\, k_a\, [S_2O_3^{2-}][NH_3] \exp(\phi_a F E/ RT) \quad (A3)$$

$$i_c = -F\, k_c\, [Cu(NH_3)_4^{2+}] \exp(-\phi_c F E/ RT) \quad (A4)$$

Where k_a, k_c are the electrochemical rate constants per unit surface area for the anode and cathode reactions respectively.

ϕ_a, ϕ_c are the transfer coefficients for reaction A1 and A2 respectively.

F is the Faraday constant.

At the mixed potential E_m, $i_{mix} = i_a = -i_c$, (A5)

Also the transfer coefficients ϕ_c , ϕ_a represent the symmetry of the activation barriers for the cathodic and anodic charge-transfer reactions. For symmetrical barriers, $\phi_c = \phi_a = 0.5$. Therefore:

$(i_{mix})^2 = -i_a i_c = F^2 k_a k_c [S_2O_3^{2-}][NH_3] [Cu(NH_3)_4^{2+}]$

$i_{mix} = F(k_a k_c)^{0.5} [S_2O_3^{2-}]^{0.5}[NH_3]^{0.5} [Cu(NH_3)_4^{2+}]^{0.5}$ (A6)

The rate of an electrochemical reaction can be related to the current i, the number of electrons n involved in the reaction and the Faraday constant F:

$R = i/nF$ (A7)

According to the one-electrode mechanism n = 1, so combine Eqs. A6 and A7

$R = i_{mix}/F = (k_a k_c)^{0.5} [S_2O_3^{2-}]^{0.5}[NH_3]^{0.5} [Cu(NH_3)_4^{2+}]^{0.5}$

$= k_1[S_2O_3^{2-}]^{0.5}[NH_3]^{0.5} [Cu(NH_3)_4^{2+}]^{0.5}$ (A8)

Where $k_1 = (k_a k_c)^{0.5}$ represents the rate constant of rate determining step in Eq. A3.

APPENDIX A6 Optimum reagent concentrations/conditions and the effect of background anions on leach gold from this work

Table A6.1 *Copper(II)-ammonia-thiosulfate system without oxygen*

Cu(II) (mM)	$[NH_3+NH_4]$ (mM)	$[Na_2S_2O_3]$ (mM)	pH	Additive concentration	Effect on gold dissolution
1.5-4.5	120-300	20-50	9.3-10		
				$AgNO_3$ 0.15mM	significant positive
				NaCl 50-330mM	positive
				$Na_2S_3O_6$ 20mM	small positive
				Na_2NO_3 20-330mM	No effect
				$Na_2S_4O_6$ 5mM	small negative
				$Pb(NO_3)_2$ 0.01mM	small negative
				Na_2CO_3 110mM	negative
				Na_2SO_3 40mM	significant negative

Table A6.2 *Oxygenated copper(II)-ammonia-thiosulfate system*

Cu(II) (mM)	$[NH_3+NH_4]$ (mM)	$[Na_2S_2O_3]$ (mM)	pH	$[O_2]$ (mM)
2.0-3.0	240	50	9.3-9.5	0.06-0.25

APPENDIX A7 Front page of the three publications with abstract

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A study of the gold colloid dissolution kinetics in oxygenated ammoniacal thiosulfate solutions

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Abstract

Colloidal gold has a characteristic absorption peak at 530 nm that can be used to monitor the extent of gold dissolution in different lixiviant systems using an ultraviolet–visible spectrophotometer. This paper reports the kinetics of the dissolution of gold colloid in ammoniacal thiosulfate solutions using oxygen as a oxidant at pH 9.3–9.5 and temperature 25–48 °C. The relative rates of gold dissolution in different lixiviant systems are in descending order: oxygen–cyanide > copper(II)–ammonia–thiosulfate > oxygen–ammonia–thiosulfate > oxygen–ammonia > copper(II)–ammonia. The predominant gold(I) species in oxygenated thiosulfate solution based on the measured potentials on gold electrode is gold–thiosulfate complex ($Au(S_2O_3)_2^{3-}$). However, the measured potentials in the absence of thiosulfate are close to the reported values for the $Au(NH_3)_4^{3+}/Au(NH_3)_2^+$ couple, which indicates that disproportionation or oxidation of $Au(NH_3)_2^+$ occurs. The initial rates of gold dissolution show reaction orders of ≈ 0.3 with respect to oxygen and ammonia, and are independent of the concentration of thiosulfate and chloride. The dissolution kinetics follow a shrinking core model with an activation energy of 25–37 kJ mol^{-1}, indicating a mixed chemical-diffusion-controlled reaction.

Keywords: Kinetics; Gold colloid; Electrode potentials; Ammoniacal thiosulfate; Shrinking core kinetic model

1. Introduction

Although the cyanidation process has been used to extract gold over the past hundred years, there is a growing interest in non-cyanide gold technology. This is largely due to the environmental and other benefits of using non-cyanide processes to treat gold ores, especially refractory ores containing copper sulfides and/or preg-robbing materials (Ritchie et al., 2001). The ammoniacal thiosulfate system with copper(II) catalyst (Eqs. 1–6) offers fast reaction kinetics comparable with cyanide (Jeffrey et al., 2001).

$$Au(s) + Cu(NH_3)_4^{2+} = Au(NH_3)_2^+ + Cu(NH_3)_2^+ \quad (1)$$

$$Au(NH_3)_2^+ + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + 2NH_3 \quad (2)$$

$$Cu(NH_3)_2^+ + 3S_2O_3^{2-} = Cu(S_2O_3)_3^{5-} + 2NH_3 \quad (3)$$

$$4Cu(I) + O_2 + 2H_2O = 4Cu(II) + 4OH^- \quad (4)$$

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Study of the Kinetics of Dissolution of Gold Colloid in Ammoniacal Copper(II) Thiosulfate Solutions

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(A J Parker Cooperative Research Centre for Hydrometallurgy, Department of Extractive Metallurgy, Murdoch University, Perth, WA 6150, Australia)

Abstract: The leaching of Gold by oxygenated ammoniacal copper(II) thiosulfate is complex due to the reactions of copper(II) and oxygen with both thiosulfate and gold. Therefore thermodynamic and kinetic studies on the dissolution of gold colloids in copper(II)-ammonia-thiosulfate lixiviant systems were carried out under nitrogen at pH 9.3-9.5 and temperature 22 - 48°C, using ultraviolet-visible spectroscopy. The difference between the standard reduction potential based on measured equilibrium potentials at a platinum electrode and those predicted on the basis of reported stability constants for the two couples $Cu(NH_3)_2^{2+}/Cu(S_2O_3)_3^{5-}$ and $Cu(NH_3)_2^{2+}/Cu(S_2O_3)_2^{3-}$ is less than 10 mV. The predominant gold(I) species based on the measured potentials at a gold electrode is the gold-thiosulfate complex $Au(S_2O_3)_2^{3-}$. The initial rates of dissolution of gold colloid suggest reaction orders of 0.4, 0.5, and 0.6 with respect to copper(II), thiosulfate and ammonia respectively. The activation energy is 40 kJ · mol^{-1}, indicating that the rate-determining step is a chemically controlled surface reaction.

Key words: kinetics; dissolution; gold colloid; ammoniacal copper(II); thiosulfate

School of Metallurgical Engineering, Xi'an University of Architecture & Technology

BENEFICIAL EFFECT OF SILVER IN THIOSULFATE LEACHING OF GOLD

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ABSTRACT

The beneficial effect of silver in gold leaching by oxygen in alkaline cyanide and thiosulfate media has been reported by previous researchers. This paper describes a preliminary study of a similar effect in thiosulfate leaching of gold by ammoniacal copper(II) at ambient temperature. Silver dissolves faster than gold in ammoniacal copper(II) thiosulfate solutions. The results based on gold colloids show that the addition of silver colloids or silver(I) nitrate has a beneficial effect on gold dissolution. The chemical controlled dissolution of gold by copper(II) is slower than the diffusion controlled dissolution of silver. The rate of dissolution of gold powder is also enhanced in the presence of silver(I) nitrate. The dissolution curves of gold colloids were analysed on the basis of a shrinking sphere kinetic model. Species distribution diagrams, electrode potential calculations, and gold and silver dissolution kinetics were used to shed more light on the surface reaction mechanism.

INTRODUCTION

Many researchers have recognized that the thiosulfate leaching of gold and silver can be a possible alternative for cyanidation, especially for pregrobbing, refractory, copper-gold, or high-silver ores/concentrates. Whilst the cyanidation is unsatisfactory in such cases, due to low gold extraction and/or high reagent consumption, there is growing concerns of toxicity, safety, and environmental issues related to the usage of cyanide. This has led to thiosulfate leaching studies with a range of different gold ores/concentrates or residues over last three decades (Berezowsky and Sefton, 1979; Zipperian et al. 1988; Abbruzzese et al. 1995; Schmitz et al. 2001; Ritchie et al. 2001; Aylmore and Muir, 2001; Kononova et al. 2001; Molleman and Dreisinger, 2002; Navarro et al. 2002; Ficeriova et al. 2002, 2004; Fleming et al. 2003; Grosse et al. 2003; Wan and LeVier, 2003; Muir and Aylmore, 2005; West-sells and Hackl, 2005). For example, the precious metals in the residue from oxidative leaching of copper sulfide concentrates in ammonia/ammonium sulfate can be subjected to cupric promoted ammoniacal thiosulfate leach (Berezowsky and Sefton, 1979). Successful attempts have also been made to recover gold from thiosulfate leach solutions using solvent extraction, ion-exchange, cementation, or precipitation (Zhao et al. 1997; Kejun et al. 2003; Nicol and O'Malley, 2001, 2002; Choo and Jeffrey, 2003; Hiskey and Lee, 2003; Navarro et al. 2004; West-Sells and Hackl, 2005). The toxicity of ammonia, effect of host minerals, preg-robbing by clay minerals, consumption of reagents due to side reactions of copper(II) with thiosulfate and/or host minerals, and the detrimental effects of the degradation products of thiosulfate and/or host minerals on downstream processing are some of the drawbacks of the thiosulfate leaching system (Aylmore and Muir, 2001; West-Sells and Hackl, 2003; Muir and Aylmore, 2004, 2005; Feng and van Deventer, 2007a). The pre-oxidation of sulfide ores with oxygen, prior to the introduction of thiosulfate, can be beneficial in some cases (Feng and van Deventer, 2007b). Research activities related to non-ammoniacal and non-copper thiosulfate and mixed thiourea-thiosulfate leaching systems using iron(III)/oxalate or EDTA as the oxidant, and anaerobic in-situ thiosulfate leaching operations, have also gathered momentum (Ji et al. 2003; Arima et al. 2004; Chandra and Jeffrey, 2005; Zhang et al. 2006; Heath et al. 2008).

Silver coexists in most gold ores in the forms of alloy electrum, acanthite (Ag_2S), or other minerals (Millard, 2005). Both fundamental and reactor leaching studies have shown evidence for faster dissolution of silver than pure gold and the beneficial effect of silver on cyanide or thiosulfate leaching of gold in oxygenated solutions (Wadsworth and Zhu, 2003; Webster, 1986). However, the extraction percentage of silver from natural gold ores is lower than that of gold during both cynidation (Hiskey and Sanchez, 1990) and thiosulfate leaching (Berezowsky and Sefton, 1979; Abbruzzese et al. 1995, Ficeriova et al. 2004). Low solubility of silver sulfide in cyanide solutions is responsible for slow extraction of silver during stirred reactor leach (Luna and Lapidus, 2000) and heap leach operations (Xie and Dreisinger, 2007). While slower dissolution of acanthite requires excess cyanide (Millard, 2005), ammoniacal copper(II) thiosulfate offers faster leaching of silver sulfides (Flett et al. 1993; Briones and Lapidus, 1998).

Rates of dissolution per unit surface area of silver, gold, and gold-silver alloys reported by previous researchers are listed in Table 1. Thiosulfate leaching of pure gold by air is much slower than cyanidation. Copper(II), which is a faster oxidant than oxygen, acts as a redox mediator in ammoniacal-thiosulfate solutions for gold oxidation (Ritchie et al. 2001). Copper(I) produced in the leaching reaction Au+Cu(II)=Au(I)+Cu(I) is oxidized to copper(II) by oxygen. The anodic oxidation of gold in non-ammoniacal thiosulfate solutions is also enhanced by the presence of copper(II) (Table 1). This has been confirmed by stirred reactor leaching tests of gold in oxygenated thiosulfate solutions at pH 12 which showed that the presence of copper in the form of ions, metal or oxide enhanced the rate of gold dissolution (Zhang and Nicol, 2005).

In the absence of other impurities, both massive and colloidal gold have comparable, but very low rates of dissolution in oxygenated (non-copper) thiosulfate solutions as shown in Figure 1 (Webster, 1986). However, the presence of silver in alloyed or colloidal form enhances the rate of dissolution of gold. Likewise, Fig. 2 shows that higher silver grades in oxide ores cause a higher extraction of both gold and silver, especially during leaching with ammoniacal copper(II) thiosulfate (Muir and Aylmore, 2004, 2005). Comparable rates of dissolution of gold from pure